VŠB-Technical University of Ostrava
Faculty of Mechanical Engineering
Department of Mechanical Technology

Analysis of the DC01 Steel's Surface Depending on the Resistance to Corrosion and the Adhesion of Metallic Layers to the Metal Structure of Medical Equipment

Doctoral Dissertation

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Doctoral Supervisor:	Doc. Ing. Jitka Podjuklová, CSc. prof. h. c.
Doctoral vice-Supervisor:	Prof. Ph.D. hab. Maciej Hajduga
Doktorand:	M.Sc. Dariusz Sołek

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ANNOTATION OF DISSERTATION

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The dissertation focused on the analysis of surface layer of steel substrate and metallic coatings applied to DC01 and RSt37-2 NBK steel, as well as the corrosion resistance of the applied coatings. Selected research materials, DC 01 and RSt37 2 NBK, are very often used in the manufacture of medical equipment such as rehabilitation beds, trolleys, surgical tables, screens and bedside cabinets.

Observations made in units of health care, permit the conclusion that the construction elements of the medical equipment are protected by paint coatings as well as metallic nickel-chrome coatings. During long-term operating and maintaining of aseptic medical equipment there is a significant reduction in the corrosion resistance of galvanized coatings. It particularly relates to areas with difficult accessibility where cleaning, despite the use of aggressive disinfectants, is not easy. These areas often contain residues of food, drink, expectoration as well as blood. All these factors have a devastating impact on the protective coating, leading to the appearance of corrosion.

The research revealed that corrosion is a favorable condition for the deposition of dangerous bacteria and fungi. Therefore, the study selected standard protective coatings (nickel-nickel-chromium, nickel-chromium) as well as antibacterial properties, nickel-copper and copper without a sublayer. The research focused mainly on the properties of selected anti-corrosive galvanic coatings. The results allow for a better choice of the protective coating when designing medical equipment in terms of protection against corrosion and bacteria.

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THE LIST OF DESIGNATIONS AND ABBREVIATIONS

Symbol	Description	Base unit
AAR	solution of acid rain	[-]
API	Analytical Profile Index	[-]
ASS	acid solution salt mist	[-]
BHI	Brain Heart Infusion	[-]
CASS	salt spray test	[-]
DC 01	steel in the form of cold-rolled sheet	[-]
E	electrode potential	[V]
E°	standard electrode potential	[V]
$E°_{anoda}$	anode potential	[V]
$E°_{katoda}$	cathode potential	[V]
E_{cp}	critical potential	[V]
EDS	energy dispersive spectroscopy	[-]
E_{K-A}	potential of the cathode-anode transition	[mV]
E_{kp}	critical passivation potential	[mV]
E_{np}	potential nucleation (initiation) pitting	[mV]
E_p	potential passivation	[mV]
$E_{st(kor)}$	stationary potential (corrosion)	[mV]
HV	Vickers hardness scale - the scale for metals marking	[-]
$i_{E=-750\ mV}$	cathodic current density at -750 mV potential	[A/cm^2]
I_{kor}	corrosion potential	[A/cm^2]
i_{kor}	corrosion current density	[A/cm^2]
i_{kp}	critical density of passivation,	[A/cm^2]
i_{kryt}	critical current density	[A/cm^2]
i_p	passivation current density	[A/cm^2]
Ir	roughness profile	[-]
ISO	International Organization for Standardization	[-]
It	the total length of the section profile	[mm]
Iw	undulations profile	[-]
1kgf	one kilogram-force (page 80 - hardness measurement)	[N]
Mr1	material part, determined by the intersection of the line separating the hills protruding from the roughness core profile	[%]
Mr2	material part, determined by the intersection of the line separating the deep recesses of the roughness core profile	[%]

NSS	neutral salt mist	[-]
P	passivation potential	[mV]
pH	quantitative scale of acidity or alkalinity of aqueous solutions of chemical compounds	[-]
PN-EN	Polish standard complies with the requirements of European standard	
R	roughness	[μm]
Ra	arithmetical mean deviation of the roughness profile	[μm]
Rk	core roughness depth	[μm]
Rp	polarization resistance	[Ωcm^2]
Rpk	reduced height of hills	[μm]
RSt37-2 NBK	circular tube welded precision annealed by	[-]
Rvk	reduced depth of the the recesses	[μm]
Rz	roughness parameter – an arithmetic mean height of the five highest hills above the line of the average reduced by the mean of the five lowest recesses below the average	[μm]
SBF	artificial blood	[-]
TAA	thioacetamide corrosion test in a humidified atmosphere containing hydrogen sulfide	[-]
t_I	current as a function of time	[-]
U_A	potential of the anode	[V]
U_K	cathodic potential	[V]
U_{kor}	corrosion potential	[V]
W_{KW}	pitting corrosion coefficient	[-]
X_2	oxidant	[-]
δ	residual stress of the surface layer	[-]
Ca	calcium	[-]
Cl	chlorine	[-]
Cu	copper	[-]
Fe	iron	[-]
H	hydrogen	[-]
N	nitrogen	[-]
NaCl	sodium chloride	[-]
NaOH	sodium hydroxide	[-]
Ni	nickel	[-]
S	sulfur	[-]
Si	silicon	[-]
SO_2	sulfur dioxide	[-]

1 INTRODUCTION

The current development of technologies in the field of metallic coatings and painting is very advanced. However, researchers are still looking for better solutions, particularly in the area of medicine and dentistry [1-4].

Observations made in health care revealed that the structural elements of the medical supplies-type operating tables, beds and bedside cabinets have protection on their surfaces in the form of galvanic coatings made of precious metals such as nickel and chrome or painting.

During an operation, the maintenance of hygiene standards and long-term use, followed by degradation of galvanic coatings as corrosion increased [5,6]. You can see the intense local corrosion in the form of "outbreaks" in locations which are hard-to-reach when trying to maintain purity. The influence of chemicals – disinfectant, for example has an effect on the spread of corrosion causing further damage to the coating (Fig. 1).

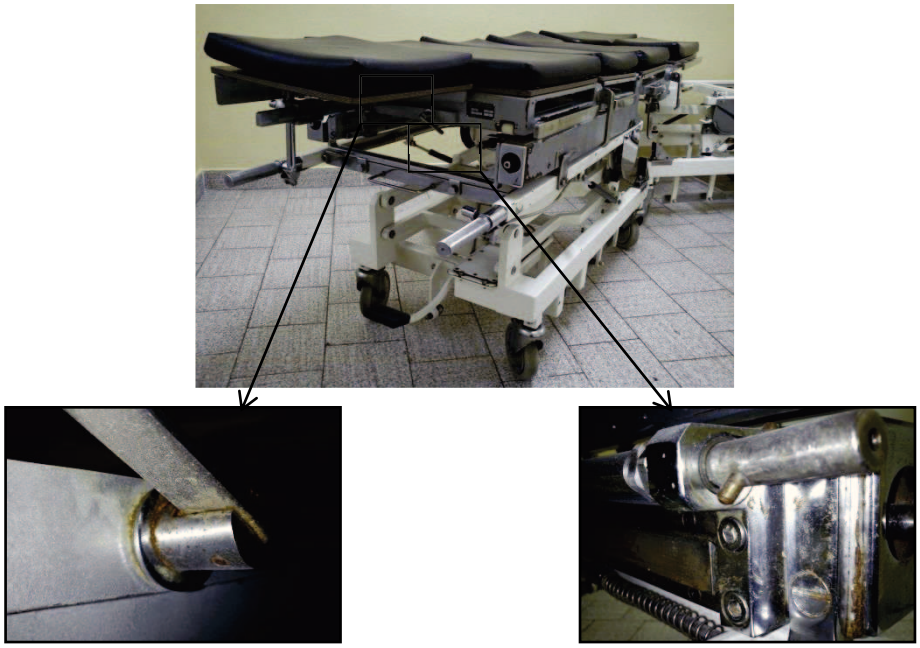

Fig.1 An operating table with the place of the corrosion [from own investigations]

The available literature does not contain a lot of information on the corrosion of the equipment used in the area of hospital usage [7, 8].

Long-term exploitation of these devices and structures in disruptive and difficult conditions, results in them also being exposed to mechanical action, and further damage to the protective coating (chromium-nickel).

In this area we also have to deal with corrosion caused by body fluids like urine, blood, saliva, sweat, etc.

The formation of "outbreaks" of corrosion and their random spread causes subsidence and growths of bacteria such as colon bacillus (Latin Escherichia coli), Pseudomonas (Latin Pseudomonas aeruginosa), Staphylococcus aureus (Latin Staphylococcus aureus) and others [9].

Placement of microorganisms in niches, void and metallic coatings with an already existing corrosion causes an electrochemical corrosion phenomena that can also be linked by microbial corrosion [10-14].

2 LITERATURE REVIEW

2.1 Characteristics of the selected types of corrosion of metals

CORROSION PHENOMENA

Corrosion is labelled as a physic-chemical and electrochemical interaction between metal material and the surrounding environment, which causes the corrosion damage which then results in a reduction of metal properties. Due to the type of reaction, causing a destruction of metal or alloys can be made by the primary division of the corrosion of metals and alloys for the chemical and electrochemical interaction.

Sometimes, corrosion is accompanied by a physical phenomena of erosion, friction or a consumption of cavitation. In such cases, the combined effects of physical and chemical factors, the phenomenon of the destruction of metals are referred to respectively as erosion corrosion (corrosion-erosion), fretting corrosion or cavitation corrosion. The basic definitions of the concepts related to the corrosion of metals and alloys contains standard PN-EN ISO 8044:2002 [15,16].

2.1.1 Atmospheric corrosion of metals

An atmospheric corrosion is an example of an electrochemical corrosion that causes the most economic damage from all known types of corrosion.. It is estimated that the cost of protection against atmospheric corrosion is about 70% of the expenditure incurred on all types of corrosion protection [17].

For atmospheric corrosion processes, the chemical composition of the atmosphere has a major impact, mainly due to its industrial pollution and climatic parameters. Along with the natural components of the atmosphere, which are essential for the progress of corrosion their is:

-*Oxygen*, which as a component of the atmosphere with a high vapour pressure of partial (about 20% of the total atmospheric pressure, as an electron acceptor and has a major impact on the corrosion of metals. Without oxygen mileage the electrochemical corrosion processes are impossible. Particularly active in the corrosive processes is the ozone concentration in the ambient air which is within $\pm$ 10 $\div$ 50 $\mu g/m^3$ [18].

-*Water*, which is third in terms of the contents of a component of the atmosphere, unlike others, is characterized by a variable, depending on the time and place of the

concentration. The water present on the surface of metal causes the creation of an electrolyte layer, which allows you to process electrochemical processes responsible for an atmospheric corrosion of metals.

-*Carbon dioxide* concentration, as a natural constituent of the atmosphere is approximately 10^{-2}%, and is characterized by a high solubility in water (0,232 g CO_2 in 100 g H_2O. a temperature of 10 ° C), with the result that it creates in the air water acidic solutions with a pH of 5,0 to 5,6 [3]. It plays an important role in atmospheric processes and corrosion of metals [19].

2.1.2 Gas corrosion

Gas corrosion in the environment that contains only dry gas, for example oxygen or air, nitrogen, sulfur and its compounds, gases and steam, is the most common example of corrosion. Chemical corrosion processes rely on the destruction of metals and alloys as a result of chemical reactions. In contrast to electrochemical corrosion chemical corrosion which runs dry, without the participation of the electrolyte.

CHEMICAL REACTION OF OXIDATION

The primary type of reaction causing gas corrosion when forming is thermal oxidation, a chemical reaction is that for the simplest case of the oxidation of pure metal divalent, can be represented as follows:

$$M + ½X_2 \rightarrow MX$$

Where:

M – metal,

X_2 – oxidizer for example, the O_2, S_2, N_2.

THE GAS CORROSION PRODUCTS

Reaction product of the oxidation usually occurs in the solid state, rarely in a liquid or gaseous state. Permanent oxidation product layers are called scales free, after a few seconds when their thickness is greater than 10 μm or tarnishes layers when their thickness is lower even after a very long time. Tarnishes layers are usually compact and are a single-phase throughout its volume. Scale free created on the surface of pure metals and alloys consists mostly of two or three layers, the outer of which, bordering oxidant, is the most compact, whereas the inside is bordering on metal-porous [10, 11] .

Corrosion damage due to an external appearance and changes in physical characteristics can be divided into several basic types (Fig. 2).

UNIFORM CORROSION

Uniform corrosion is almost monotonous all-over metal damage over a period of time (Fig. 2a). A uniform corrosion rate is given in mm/year, and sometimes also in mg/dm^2 · day. The metals or alloys with a uniform corrosion rate of no more than 0,15 mm/year can be applied to particularly exposed corrosive destruction of equipment elements responsible, for example valve internal combustion engines or rotors pumps.

When the rate of corrosion of a uniform is greater than 1,5 mm/year, it is such that metals and their alloys may not be applied to the elements exposed to the corrosive destruction equipment.

LOCAL AND PITTING CORROSION

Local corrosion is characterized by the diversification of destroying speed metal or alloy in different areas of its surface. An example of such failure is corrosion pitting (Fig. 2b). The ratio of the largest to a depth of pitting depth, resulting in the loss of mass in the sample, is called pitting corrosion factor W_{KW} (for uniform corrosion $W_{KW} = 1$). Another example of localized corrosion is the so-called knife corrosion occurring in a narrow border zone between the parent material and weld or solder.

SELECTIVE CORROSION

Selective corrosion is the destruction of one or more phases of the alloy at a much greater speed than the speed of the warp alloy damaging. As a result, a porous residue of the product retains its shape, but his endurance is greatly reduced. Selective corrosion occurs, inter alia, noble metal alloys (e.g. Au-Ag and Au-Cu), gray cast iron (corrosion of metallic phase is, and remains, graphite), and an example of this phenomenon is the dezincification brass (Fig. 2c).

INTERCRYSTALLINE CORROSION

Intercrystalline corrosion (Fig. 2d) runs mainly on the borders of the particles of metals or their alloys, with a very high speed, and reaching large depths. Intergranular

corrosion often causes catastrophic damage as a result of a significant reduction in the strength and ductility of the metal, with no clearly visible symptoms externally.

CORROSION STRESS AND FATIGUE

Corrosion cracking is caused by the simultaneous action of corrosion and tensile stress, environment variables or constants (Fig. 2e). When the metal or alloy subjected to constant tensile stress operates environment corrosion, stress corrosion and cracking occurs. Tensile stress causing stress cracking can be applied from the outside or the inside and has caused plastic working, heat or welding. It is subjected to alternating tensile stresses, fatigue may corrode in a case when a metal immersed in corrosive environment, is subjected to alternating tensile extending, it could result in corrosion fatigue [10, 20] .

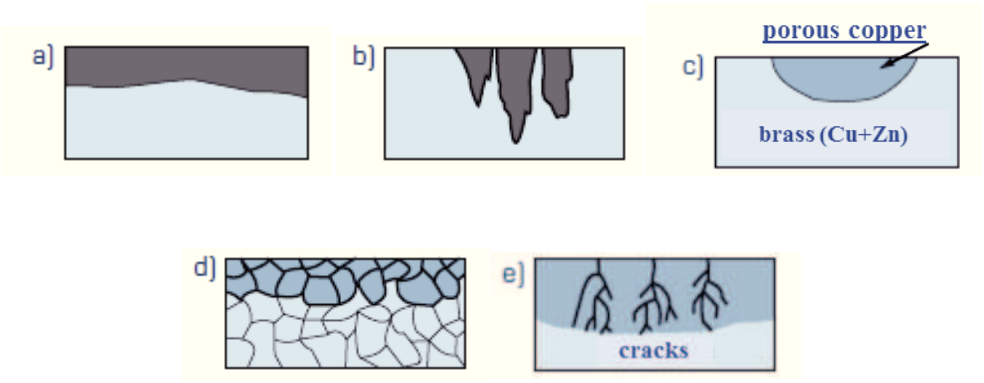

Fig.2 *Typical corrosion damage-blackened area covered by the zone shows a kind of corrosion:* ***a)*** *uniform corrosion,* ***b)*** *pitting corrosion,* ***c)*** *selective corrosion,* ***d)****intercrystalline corrosion,* ***e)*** *corrosion cracking [15]*

2.1.3 Electrochemical corrosion

ELECTROCHEMICAL CORROSION MECHANISM

Most corrosion processes are electrochemical. The surface of any metal or alloy can be thought of as a collection of positive and negative electrodes, short compact by (Fig. 3). Between these electrodes, which are the elements of the structure of metals or alloys, there is a difference of potentials. When the metal is threated by the electrolyte, which can be water or aqueous solutions of salts, acids and alkalis, displaying the local micro-cell and the local flow of electric current. This is accompanied by chemical reactions reduction and oxidation.

A chemical reaction reduction (cathodic reaction) occurs on the electrode called the cathode and is related to the flow of a positive solution of current contractual electrolyte to electrodes (that is, in fact, electrons flow in the opposite direction), for example:

$$Cu^{2+} \rightarrow Cu - 2e^{-}$$

The electrode called the anode oxidation chemical reaction proceeds (anodic reaction) connected with the movement of positive electric charges from the electrode to the electrolyte, for example:

$$Zn \rightarrow Zn^{2+} + 2e^{-}$$

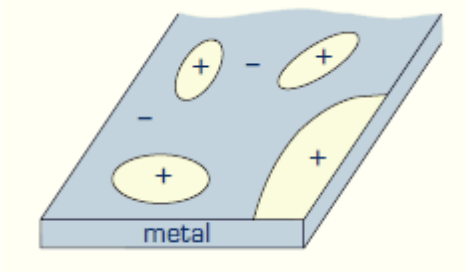

Fig.3 *An arrangement diagram of the local corrosion cells on the surface of the metal [15]*

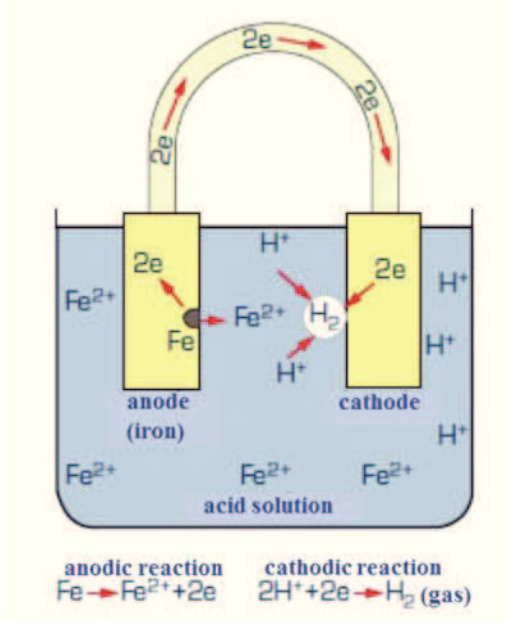

Fig.4 *A diagram of the processes taking place on two electrodes during the corrosion of iron in acid solution (according to A.G. Guy) [15]*

Whilst the flow of electric current is occurring so does the flow if ions, wherein cations such as H^{+}, Fe^{2+}, tend to cathode, while anions e.g. Cl^{-}, OH^{-}, SO_4^{2-}, tend to anode.

As a result of electrochemical processes occurring in the micro-cells on the surface of the metal of electrolyte subjected to the action, the process of the corrosion runs. Corrosion occurs only on anodes micro-cells where salts or hydroxides of metals deposited on the electrode or passing through to the solution usually form (Fig. 4). During the corrosion of the positive and negative electrode, surfaces continuously change their position. Thus, galvanic corrosion can also be uniform.

TYPES OF CELLS ELECTROCHEMICAL CORROSION

Cells from the surface of metals or alloys, deciding on a course of electrochemical corrosion may be from the three kinds, thou usually a combination of two or three cell types.

Cells of different electrodes formed in contact with other elements of two different metals and alloys, or connected parts of the same metal, one of which is crushed, and the second - annealed. Microcells are also formed in alloys and multiphase polycrystalline metals. Microcells may be, for example contaminants, inclusions of, various alloys phases, and even the same phase grains with different crystallographic orientations.

Concentration cells are formed identical to electrode, immersed in electrolytes with different concentrations. Salt Concentration cell consists of two electrodes, for example, copper, immersed in an aqueous solution of salt (e.g. copper sulfate) at different concentrations in the vicinity of each of the electrodes. As a result, reactions taking place at the electrodes occurs a striving force to compensate for the concentration of the two solutions.

Cell concentration, oxygen is the cause of pitting corrosion of numerous metals and alloys resistant to corrosion in other environments. They are formed by two identical electrodes, such as iron, immersed in a dilute aqueous solution of salt (e.g. sodium chloride) at the same concentration, but to different degrees saturated with oxygen. This mechanism explains the crevice corrosion on the border of two parts connected by a screw connector, the formation of pits under a layer of corrosion products, sediments iron, low carbon steel (deposit corrosion) or on the boundary of phases of water – air on the products of carbon steel immersed in water (corrosion on the line water).

Differentials cell temperature of the electrodes are composed of the same metal, but with different temperature, immersed in an electrolyte of the same chemical composition. Such cells are predominantly found in steam boilers, radiators and heat exchangers.

PROGRESS OF ELECTROCHEMICAL CORROSION FACTORS

The tendency for the metal or alloy electrochemical corrosion increases with the increase of the electromotive force of cells corrosion. Metals tidied in the so called electromotive series by the dwindling of the standard electrode potentials, namely equilibrium potential of the metal with ions it's the unit activity (Table 1). Among the metals constituting the anode corrosion cell is a metal with a lower standard electrode potential, exhibiting greater activity, and hence greater susceptibility to corrosion. For example - the iron in an aqueous solution of Fe^{2+} having an activity equal to a unity is in balance with the potential of -0,44 V. In the case of a connection conductor of electricity iron with copper tend to have an increase in the potential of iron. Then the electrochemical process occurring involves Fe^{2+} ions move toward the electrode with a greater potential then what is tantamount to the corrosion of iron (Fig. 5). But when iron is electrically connected to the zinc, ions Fe^{2+} from the solution tend to reduce on iron (Fig. 5).

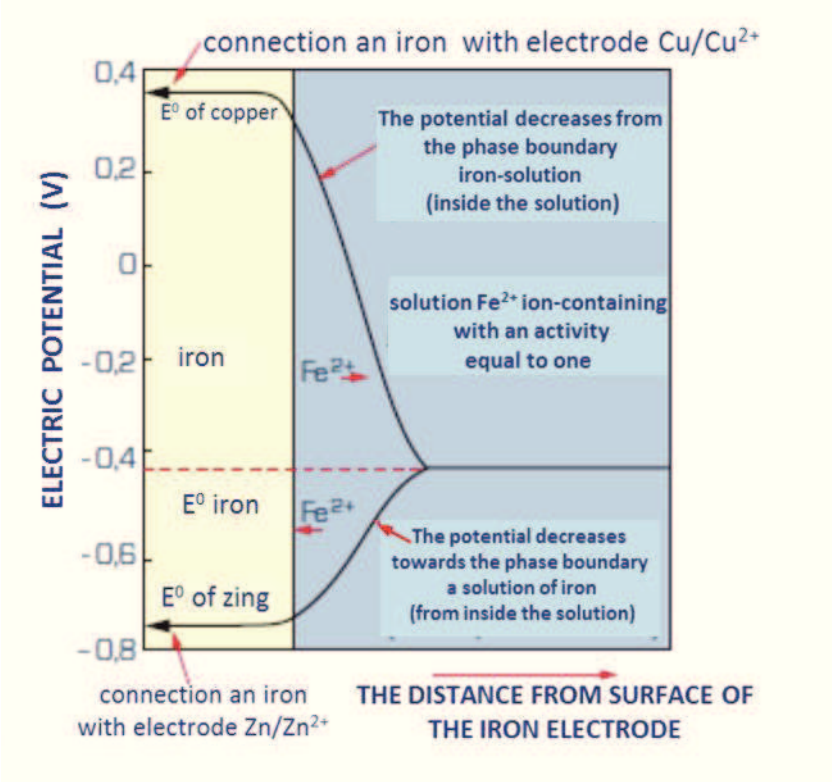

Fig.5 *Changes in cell oxidation potential, iron-copper and iron-zinc [15]*

The actual activity of the ions in equilibrium with the metal outside a standard electrode potential, greatly depends on the type of environment. Some of the environments such as strong base and cyanides, contributes to reduce the activity of ions in equilibrium with the metal, causing a shift to a higher electrode potential, and even positive values.

The cause of increasing the electrode potential may also be the formation of a passive layer of surface. For this reason, in the specialized literature there is published to the ranks of the tension of metals and alloys in specific environments, for example: in seawater, including metals and their alloys technical active and passive, and also welding and adhesives used for their merger.

Table 1 Electrochemical series of selected metals [15]

Reduction half reaction	**The standard electrode potential in temperature 25 °C - E° [V]**
Strongly oxidizing	
$Ag^{2+} + e^- \rightarrow Ag^+$	+1,98
$Au^+ + e^- \rightarrow Au$	+1,69
$Au^{3+} + 3e^- \rightarrow Au$	+1,40
$Ag^+ + e^- \rightarrow Ag$	+0,80
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0,77
$Cu^+ + e^- \rightarrow Cu$	+0,52
$Cu^{2+} + 2e^- \rightarrow Cu$	+0,34
$Cu^{2+} + e^- \rightarrow Cu^+$	+0,15
$Fe^{3+} + 3e^- \rightarrow Fe$	-0,04
$Sn^{2+} + 2e^- \rightarrow Sn$	-0,14
$Ni^{2+} + 2e^- \rightarrow Ni$	-0,25
$Fe^{2+} + 2e^- \rightarrow Fe$	-0,44
$Cr^{3+} + 3e^- \rightarrow Cr$	-0,74
$Zn^{2+} + 2e^- \rightarrow Zn$	-0,76
$Mn^{2+} + 2e^- \rightarrow Mn$	-1,18
$Ti^{2+} + 2e^- \rightarrow Ti$	-1,63
$Al^{3+} + 3e^- \rightarrow Al$	-1,66
$Li^+ + e^- \rightarrow Li$	-3,05
Strongly reduce	

The galvanic cell electromotive force of the cell is the difference of the standard electrode potentials, calculated using the formula below [21, 22]**:**

$$E^\circ = E^\circ_{cathode} - E^\circ_{anode}$$

where :

E° – potential cell

E°_{catode} – cathode potential

E°_{anode} – anode potential

ENVIRONMENT CONDUCIVE TO ELECTROCHEMICAL CORROSION

Electrochemical corrosion of corrosive environment also decided. The mechanism of electrochemical corrosion can occur not only in the case of the impact of electrolytes, which are aquatic environment or aqueous solutions of acids, salts and bases. Electrochemical corrosion are also metals and alloys burrowed in the soil, often subjected to stray currents. The sources of stray currents can be electric railways or trams, electric welding equipment, electroplating and power lines earthed with an alternating current.

DIFFUSION POTENTIAL

The potential difference between two electrodes immersed in an electrolyte algebraically summed with the diffusion potential (also called a liquid), is namely the potential difference formed between solutions of a different concentration or chemical composition, in which each electrode is immersed. The value of potential of diffusion is dependent on the relative difference in ion mobilities and their concentrations at the border of the solutions.

POLARIZATION

In terms of the electrochemical corrosion potentials electrodes forming corrosion cells often change as a result of the current accident to or from the electrode, causing the reduction of a potential difference between the electrodes of the cell. The value of the potential changes is called polarization.

Causes of polarization as a result of corrosion cells may be:

- concentration polarization, caused by the change of the surface concentration of active ions in the electrode as a result external corrosion current flow,

-activation polarization caused by the slow course of the reaction on the electrode corrosion cells, requiring certain activation energy, for example overvoltage hydrogen evolution in cathode areas on the metal surface,

- a drop in potential and as a result the resistance of the electrolyte changing their chemical composition near the electrode, or increasing the resistance of the surface layer electrode due to deposition of corrosion products on it.

When polarization occurs primarily at the cathode, the cathode is controlled (Fig. 6a), while at the anode - anodically (Fig. 6b) when it is even on both electrodes – it is a mixed polarization control (Fig. 6c). If the electrolyte resistance is very large, so that there is no electrode polarization, it resists control (Fig. 6d). Polarization reduces corrosion speed.

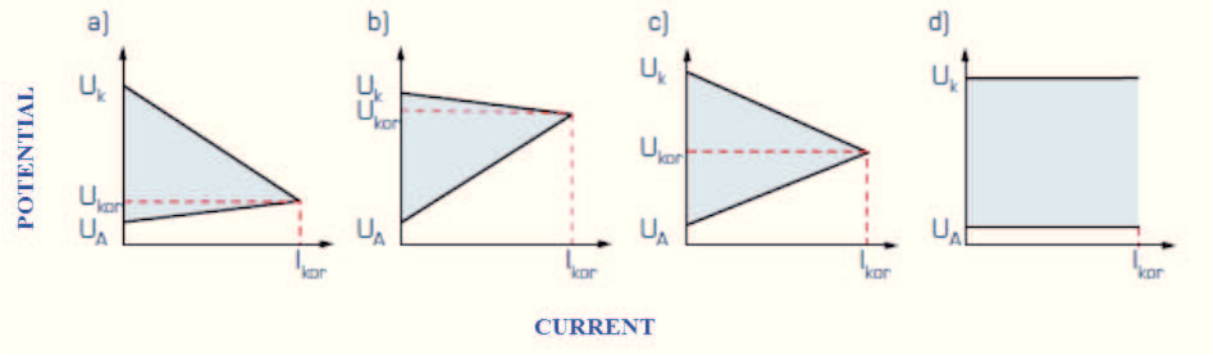

Fig.6 A polarization control scheme during electrochemical corrosion: a) cathode b) anode c) mixed d) resistance, UK, AU - potentials, cathode and anode, respectively, U_{kor} and i_{kor} - respectively the potential and corrosion current [15]

PASSIVATION OF METALS AND ALLOYS

Electrochemical properties of the metal characterized by a negative potential to the electrode having high activity in a series of voltage or an alloy consisting of such metals sometimes properties correspond to those of precious metal or those less active. This condition is called passive. Passive metals or alloys have very little galvanic corrosion. For these metals which includes, for example chromium, nickel, molybdenum, and alloys passive are, for example passive steels and corrosion resistant monel (70% Ni, 30% Cu).

The theory oxide layer assumes that the passive metal oxide layer decides on the hermetic surface or any of the other compounds forming of metal, and separating them from the corrosive environment by preventing the diffusion of corrosion products into the metal.

Adsorption passivation theory assumes that the metal passive is covered with a layer of chemicals adsorbed, for example: oxygen, the booster anode nodal operation. This layer provides a barrier that is diffusion.

POTENTIOSTATIC POLARIZATION CURVES

The passivation of metals and alloys is characterized by the potentiostatic polarization curve, obtained from potentiostat that specifies the relationship polarization current and electrode potential of the investigated metal which is relative to the standard reference electrode. For example - potentiostatic anodic polarization curve of iron in normal aqueous a sulfuric acid solution is shown in Figure 7 The potential is lower than the potential of the passivation P of iron although Fe is active, corrosive anodically to Fe^{3+}. Increasing the potential to a value P, which corresponds to a critical current density i_{kryt}, causing a jumping decrease in the current density to a value corresponding to a current density of passivation

i_{pas}. A further change in the value of the equilibrium potential, about 1,7 V, does not change the current density, and the corrosion products are the Fe^{3+} ions in the compounds in the form of a very thin passive film.

The substantial increase in electrode potential than the equilibrium value, so called, over potential of oxygen evolution, causes an increase in the oxygen evolution, which is related to the corrosion rate which is significantly higher than the lower potential of the electrode. This phenomenon is called transpassivity [23].

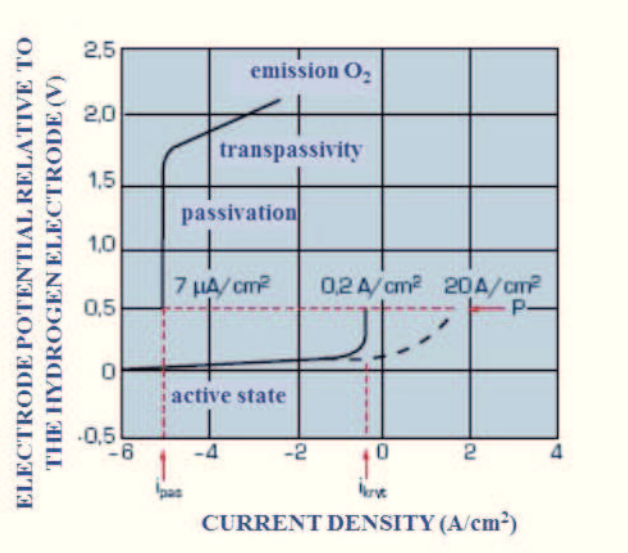

Fig.7 *A potentiostatic anodic polarization curve of iron in a normal H_2SO_4 solution (according to K. Bonkoeffera)[15]*

2.2 A study of corrosion resistance, electrolytic coatings

Corrosion resistance is a feature that primarily determines the suitability of coatings for corrosion protection in the foreseeable conditions of use. A corrosion test of both coatings and metal rely on samples of its action more or less of natural or artificial composite corrosion environment, which the components interact chemically, electrochemically and mechanically to metal or a protective coating.

2.2.1 Corrosion studies laboratory-accelerated

Accelerated studies are carried out in selected laboratory conditions so that the corrosion process could go faster than under natural conditions. Application of the corrosion factors must be kept in such limits to avoid changing the nature of the corrosion process.

An acceleration of the corrosive damage is usually achieved by increasing the intensity of the action of the corrosive agents.

Most of the test methods (standard) tests in chambers, the use of electrochemical corrosion test methods make it possible to gain a greater acceleration of corrosion. The discussion of the relevance and the selection of the test methods of corrosive where given by, among others: Biestek [24,25], Biestek, Kalinowska, Hitczenko [26], Schulz [27], Chojnacka-Kalinowska and Hitczenko [28].

2.2.2 The methodology selected studies of the accelerated corrosion

CLIMATE RESEARCH

In studies of climate changes in temperature, humidity and the results of a condensation of steam on the surfaces of the samples are seen as aggressive corrosive factors

These factors occur in the conditions of use of metals and coatings. Types of agents and their intensity are different and changing over time. A study of the accelerated climate should play with naturally occurring agents.

Climatic tests conducted in the chambers of corrosion, in which the humidity and temperature of water vapor are properly regulated.

Climatic tests can be carried out at a constant temperature and humidity, and by periodically changing the parameters. The duration of studies generally depends on the type of products, test equipment and the foreseeable conditions of use-the most common are 2, 7, 14, 21, and 56 days.

RESEARCH IN ARTIFICIAL ATMOSPHERES

Researches in artificial atmospheres rely on subjecting the tested products in addition to an atmosphere contaminated with chemical gas is an accelerating corrosion processes. These tests are carried out with increased humidity and sometimes with an elevated

temperature. General requirements for tests in artificial atmospheres are given a standard PN-EN ISO 7384:2001.

The most common and the most commonly used types of studies are in the humid atmosphere of the impure sulphur dioxide (SO_2). The manner of conducting research contains the standard PN-EN ISO 6988:2000.

Research in to the atmosphere of sulfur dioxide is discussed in several publications [29-33].

To research in a humidified atmosphere containing hydrogen sulphide a thioacetamide -*TAA* test is used and according to standard PN-EN ISO 4538:2001 replaced the standard PN-84/H-04615. This research is carried out in an atmosphere containing hydrogen sulphide emitted with thioacetamide in a chamber in which the relative humidity is 75% and the temperature is 20 ± 5 °C.

This type of test is also carried out in the atmospheres of one or more of the polluting gases of low concentrations and is also carried out using specific conditions of temperature and relative humidity according to the PN-EN ISO 10062:2008. These tests apply to the study of metals and their alloys and certain metal coatings (anode and cathode), organic and conversion.

RESEARCH IN TO FOG SOLUTIONS

One of the most commonly used method is the accelerated test method in the mists of solutions, also the method of salt mist test, which has been used for decades to study the corrosion resistance of metals and coatings can also be classed as a commonly used method.

Salt mist tests are based on placing the samples in the chamber (the salt spray chamber), which is sprayed continuously or periodically, the solution of sodium chloride in distilled water (usually 5 or 20 per cent.). The exact conditions for the implementation of the study are standardized.

Research in the salt mist test, which depending on the type of coating and the performance of the tests can be used in three major modifications, as follows:

1) research in the neutral salt mist (NSS),

2) research on acid salt mist (ASS),

3) CASS research in solution (CASS).

Modifications to the method of salt mist testing, so-called. ASS and CASS method so far are primarily used to study the corrosion resistance of selected types of coatings. The ASS method is often used to test the metal-coating of aluminum on sends anode.

The CASS method is applied to the research of nickel-chromium, copper-nickel and chromium on external automotive parts. This method is faster than the neutral salt mist test methods and according to some authors, you get a better correlation with the results of studies in natural conditions.

CORRODKOTE METHOD

The corrodkote method is carried out in accordance with PN EN ISO 4541:2000. This method has a particular application for testing protective decoration coating copper-nickel-chromium and nickel-chromium on external automotive parts which are made of steel or cast iron with zinc alloys exposed to the direct action of mud and snow.

The research method Corrodkote relies on imposing on the surface, pastes, having moved back the components of mud and dirt from the street, and then place the research elements in a humidity chamber (climate).

The test sample is placed for 20 hrs in the chamber, in which the temperature is 37 ÷ 39 °C and the relative humidity 90 ÷ 95%.

According to the literature method Corrodkote gives repetitive results, which shows a relatively good correlation with the results of the natural conditions.

ELECTROCHEMICAL STUDIES

Electrochemical methods are the subject of many formerly conducted researches and due to the possibility of obtaining information on the corrosion resistance of metals and protective coatings in less time than on the basis of the previously discussed studies [34-37]. 35,36,37]. For the measurement of the speed of corrosion of metal coating the method seems to be the most useful in the analysis of the polarization curve near the corrosion potential, allowing for the calculation of the corrosion rate in your environment as a corrosive loss of mass test of metal in the unit of time.

Basic electrochemical studies rely on:

-recording polarization curves anodic and cathodic resistance methods, extrapolation Tafel, polarizing of the inflection of the curve of polarization. It also serves to determine the corrosion current density and speed of general corrosion of metals and alloys in a specific environment,

- recording polarization curves anodic especially useful for studies of metals and alloys in order to determine the corrosion rate in the passive state, the passive range and the capacity of the building pitting,

- maintaining a constant anode potential for accelerated tests of stress and intergranular corrosion, and to test corrosion inhibitors and metal coatings [29] .

Curves showing the dependence of the potential of the electrode of DC passing through the phase boundary metal-electrolyte, that is, curves, allow for the designation of corrosion current density of the layout. Due to the applied research technique for polarization curves are divided into:

-potentiokinetic (potentiodynamic), the electrode potential E is changed over time in accordance with a given program, and current i_z (constant current) is recorded as a function of the potential E,

- galvanokinetic, in which the external current i_z changes over time according to a specified program, and the electrode potential E is recorded in the current function i_z ,

- potentiostatic, in which the applied electrode potential has a fixed value of E, and current i_z is recorded as a function of time t_I,

- galvanostatic, in which an external constant current is tested and changes of the electrode potential E is as a function of time t.

For example, the potentiodynamic curve anodic polarization of stainless steel in a solution containing Cl^- ions can be distinguished by characteristic potentials (Fig. 8).

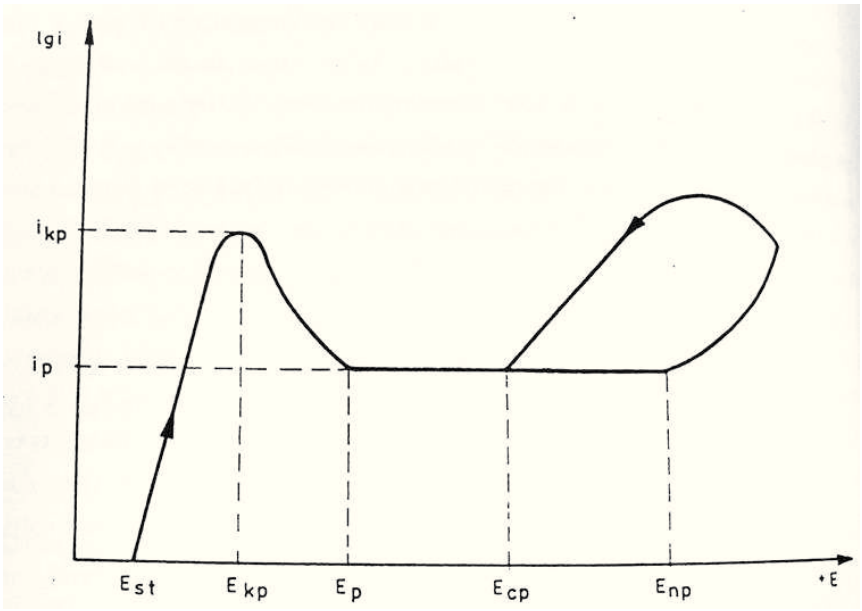

Fig.8 *A potentiodynamic curve anodic polarization of stainless steel in a solution containing chlorides [32]*

The polarity of stationary potential was in the direction of the positive potential changes at a specific rate. Once you reach a certain value, the direction was reversed to

polarity potential. Obtained in this way, the curve of the back, which does not coincide with the original curve at a certain episode. The point of the intersection of the two curves correspond to the critical potential - pitting corrosion E_{cp}.

The empowerment potential of pitting the E_{np}, located near the point of collapse to the anodic polarization curve. Pitting initiation may only occur with more positive potentials of the E_{np}, but when their is more negative potentials from E_{cp} pitting corrosion does not occur, and the existing pits are repasivation.

The size of the E_{cp} depends on the type of metal and electrolyte composition, and it does not depend on the experimental procedure. The value of the E_{np} which to a large extent depends on the type of the applied measurement technology, as well as the state of the surface of the sample.

Other characteristic points on the anodic polarization curve are as follows::

$E_{st(kor)}$ - retaining the potential for stationary (corrosive) electroless plating conditions

E_{kp} - critical passivation potential at which the anodic current density, and thus the rate of dissolution the metal reaches its maximum value,

i_{kp} - critical density passivating,

E_{kor}-E_{pc} - active area, in which the metal is corrosion,

E_p - passivation potential at which the metal changes from the active state to the passive state, the speed of anodic dissolution of the metal achieves a minimum value called passivation current density,

i_p - passivation current density [32].

In practice, the course of the anodic polarization curves may differ from the exemplary curve depending on the condition of the structure, composition substrate and the environment [29].

3 SURFACE COATING OF METALLIC MATERIALS

The primary object of study, build, operations (in the manufacturing process) and of wear (in the process of exploitation) is the surface of a solid. Solid surfaces have a different structure and properties compared to the core material. This difference is mainly due to:

- a separate energy state, as a result, there is a higher status and increased surface energy adsorption activity [38],

- overlapping influences of mechanical, thermal, electrical, physical and chemical properties on the surface during the treatment of the subject,

- cyclic: mechanical, thermal, chemical and physical influences surrounding the object medium to the surface of the object during usage.

The surface affects substantially the useful properties of objects and products. A range of physico-chemical phenomena, such as: chemical catalysis, corrosion, wear and tear (abrasive, adhesive, adhesive-abrasive, erosion, cavitation, fatigue, by oxidation, by peeling), adhesion, adsorption (physical and chemical), and flotation depends on what shall be made on the surface of the material or its participation [39].

The concept of a surface is difficult to precisely define and understand. Usually, the concept of a surface is defined differently and ambiguously - depending on the discipline of science and technology for the purposes of which it is used.

In force since 1987 the Polish Standard PN-M-04250: 1987 (Surface Layer Terminology) does not distinguish the concept of coatings, including the term "surface layer". The coating may comprise of a surface layer, superimposed on another, previously formed or produced, the surface layer. This is blurring the important differences (in terms of the properties construction, manufacture) between typical conventional surface layers and coatings.

Therefore, the distinction between the concepts adopted: the surface layer and coating, which then are assigned to them the general name - the surface layers (Fig. 9) [40-43].

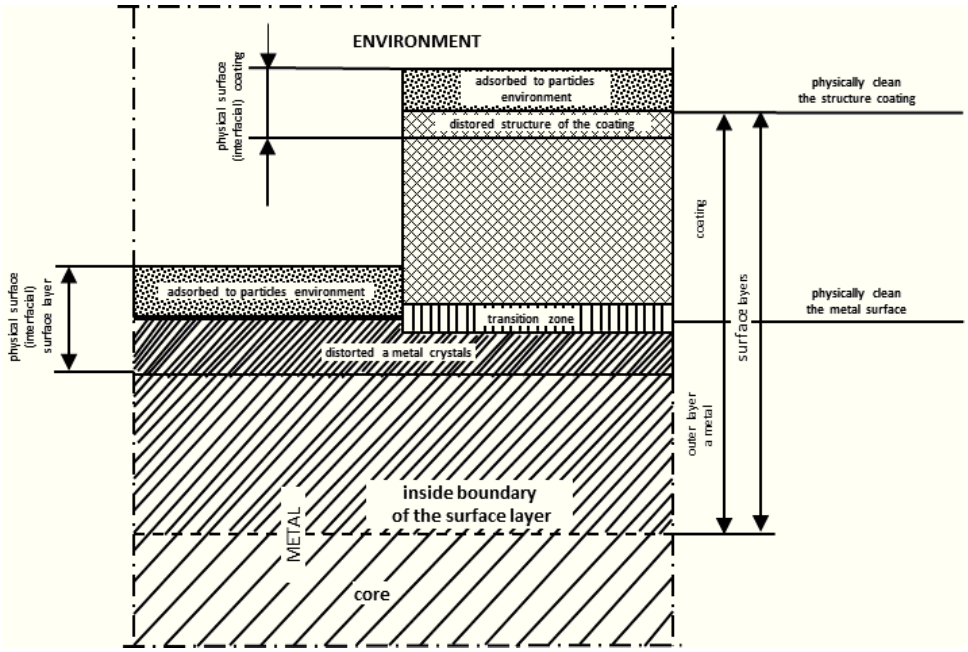

Fig.9 A schematic representation of the surface layers [32]

The narrower, close sense of the word - is the physical surface interphase area (interphase area) solid - gas (liquid), more - shall include a the surface layer, in a very broad - Also coating. The surface layers are broadly understood as a physical surface.

As the coating is made from a different material than the core, it is essentially imposed on the other core material (the surface layer). Thus, the coating has its own physical surface.

THE CONSTRUCTION OF THE SURFACE LAYER

The surfaces of solids are always a reflection of methods for their form, e.g. crystallization (the smelting and casting of), deformation (the treatment of plastic) deformation and heat influence (by the machining), diffusion (the thermochemical treatment). Every surface, regardless of how it is formed, is characterized by a certain state of inequality.

The geometry of a surface, including the surface irregularities depends on the type of machining operation. Surfaces machined by turning, grinding and polishing, show a distinct traces processing (mapping the shape and route tools) in the form of repeated irregularities. Even the most accurately machined surfaces are irregularities in height 0,01-0,1 μm, roughly squared - even more than 1000 μm (e.g. after turning coarsely ductile materials thickness of the surface layer than 1000 μm [33, 36]**.**

The shaped surface layer is always construction and the properties depend on the type of core material (chemical composition and physico-chemical properties), and the type and parameters of the machining operations. Because for the specified factor of first core material

can be very different, and may also be associated with machining operations, while the second can be varied within its wide borders - it is difficult to establish an overall regularity of the structural surface layer, a general model of the structure surface layer.

For example, models surface layers after machining differ mainly in the degree of detail, taking into account the number of different phenomena. They share however the stratified construction: a multi surface layer which consists of several, often imperceptibly crossing one into the other with different structures and properties, called zones of the layers.

The easiest, three-zone model is proposed by Kolmana1) [33] which in addition to the construction given pictorially factors characterizing the surface layer of solids - Figure 10

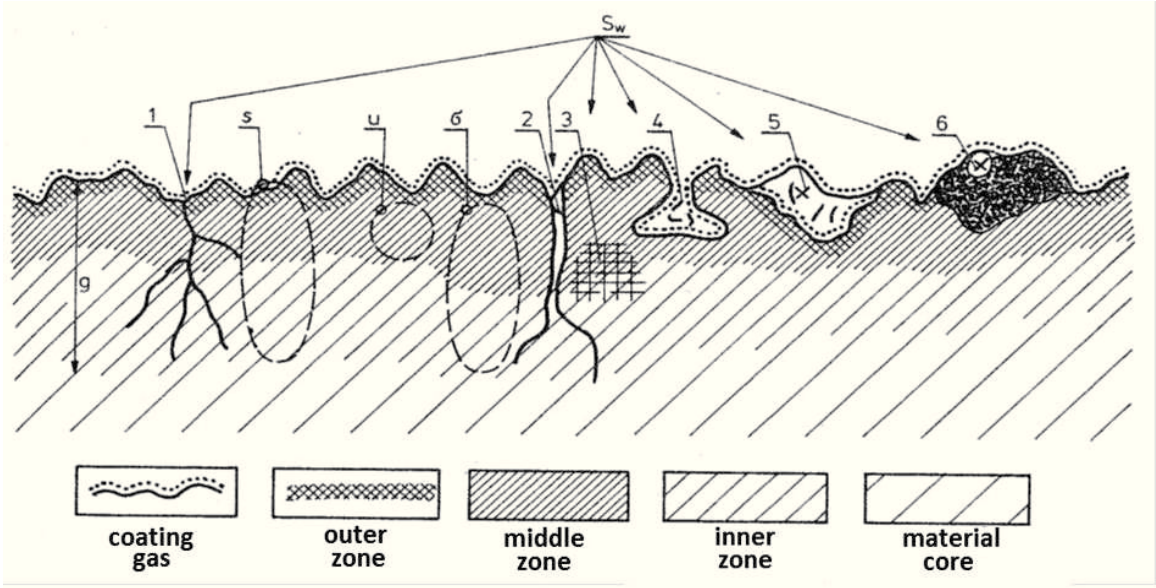

Fig.10 A schematic diagram of the set of factors characterizing the solid surface layer on the background of the three-zone model, the construction surface layer: g - thickness surface layer, s - the structure surface layer, u - strengthening (central zone), δ - internal stress surface layer, SW - contaminated surface layer, 1 - micro-crack, 2 - slot, 3 - micro-shrinkage, 4 - leeks, 5 - breach, 6 – inclusion [33]

[1)] In discussing, the proposed model was used by the Author, the original nomenclature.

The outer zone (surface layer) is a layer of particles of foreign origin (material particles anti-surface tool or friction, cutting fluid, grease, sweat, dirt, dust, etc.) sapling particles mixed with the core material. The outer zone is covered from the surrounding medium layer of adsorbed gases: oxygen, nitrogen and water vapor. The thickness of the outer layer is 0,001-0,02 μm coating gas - about $(2\text{-}3)\cdot 10^{-4}$ μm.

The central zone (layer on the surface) consists of strongly crushed grains of the core material and in many cases can be clearly textured. Thickness ranges from 0,5-500 μm. From the construction of the zone there are mainly physical properties of the surface.

The inner zone (subsurface layer) consists of a particle which is not deformed plastically, but having a structure different from the material of the core, e.g. as a result of the changes taking place under the influence of heat. The inner zone is back to internal stress. The inner zone passes the core in an elusive way. Her thickness can be up to several thousand microns [34]**.**

THE GEOMETRIC STRUCTURE OF THE SURFACE

The stereometric structure surface of the material at a specific construction is dependent on the structural machining operation. It constitutes kinematic-geometric representation.

A stereometric structure of the surface layer affects a very significant effect on the operating features: resistance to wear by friction (friction force and the lapinng time), connections to the contact stiffness, fatigue resistance, thermal conductivity, emissivity, flow resistances and tightness [44,45].

UNEVEN SURFACES

A stereometric structure forms surface irregularities, the hills and recesses that are usually the footsteps machining or consumption (Fig. 11).

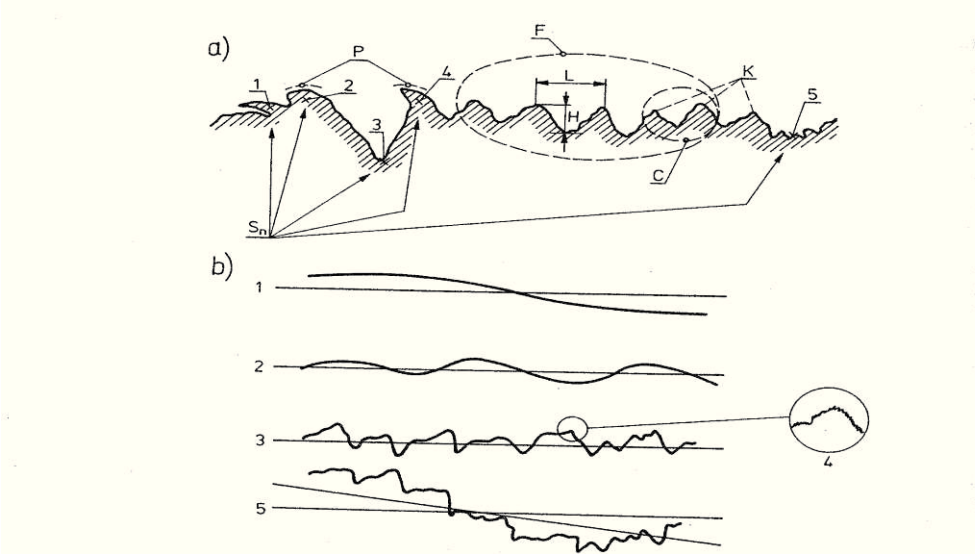

*Fig.11 Schema: **a)** contour irregularities surface solid matter [31]: **H-** height irregularities, **L-** irregularities gap, **F-** undulation, surface roughness, **P-** adhesion, **K-** orientation irregularities, **Sn-** contamination of irregularities, **1-** exfoliation, **2-** folding, **3-scratch, 4-burr 5-** pit, **b)** elements and the resultant surface roughness: **1-** the shape error, **2-** undulation, **3-** roughness **4-** sub-micro irregularities surface, **5-** is the resultant of the actual surface structure [46]*

Surface irregularities are directly involved in the interaction surfaces with a liquid medium or gas which surrounds the object or is in contact with the anti-surface inequalities.

Surface irregularities parameters determine the roughness, undulations and defects of the geometric structure.

Profile observed (measured) surface is the line of the intersection surface of the plane observed at the specified position relative to the nominal surface (referred to drawing or technical documentation without roughness, waviness and form errors) (Fig. 12).

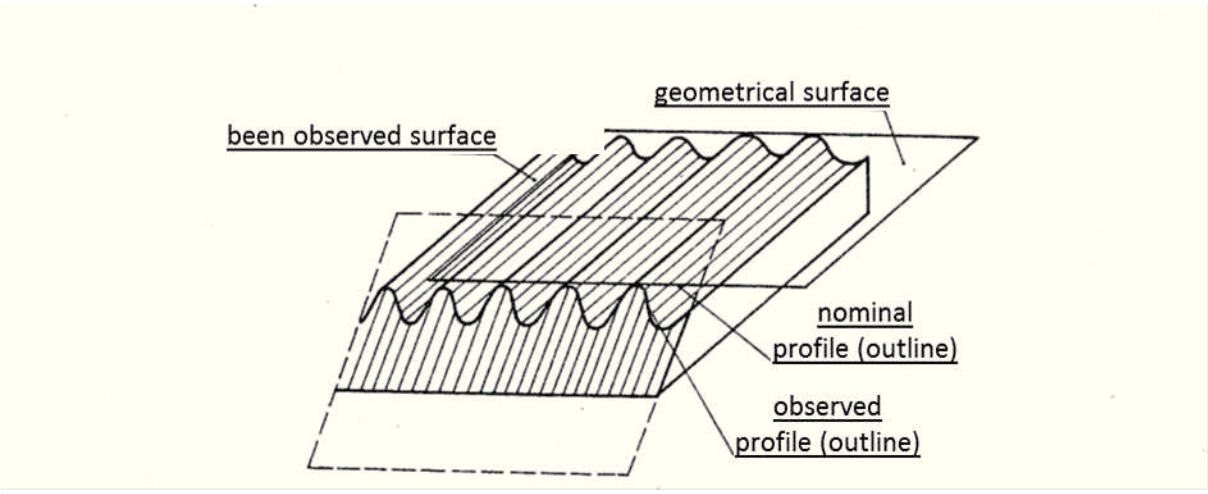

Fig.12 A nominal profile and the profile observed [47]

For the definition of the parameters of the surface roughness and surface undulations profile uses the concepts in the standards PN-EN ISO 4287:1999, PN-ISO-3274:2011.

The most important are:

-surface profile-profile obtained by the intersection of the surface of the object of the specified plane

- traced profile - the locus of points mapper tool tip center of the perfect geometric shape (countersunk with the apex spherical) and nominal dimensions, moving the surface in a cross-sectional plane,
- reference profiles - line mapping movement of the sensor along the plane of the longitudinal section of the guide,
- total profiles digital profile form a mapped relative of a reference profile, with assigned mutually verticals and horizontals coordinates,
- filter profile — a filter that extracts (separates) components of a short or long-term surface profile
- filter profile L – a filter, which marks the transition from the roughness to the components of even the smaller wave lengths present on the surface,

- filter profile Xc - a filter that determines the transition from the roughness of the waviness,

-filter profile Xf - a filter which determines the transition from the waviness components of more longer wave lengths occurring on the surface,

- primary profile — the total profile as the filter, which separates the components of a wave length shorter than the surface roughness,

- roughness profile – a profile obtained from the original profile by separating the components of the long-wave filter profile λα,

- waviness profile — a profile obtained from the profile of the original by another application profile filters separating the components of a long-wave profile (at wave lengths longer than the wave) and Ac components separating short-wave profile (roughness)

- sampling length: for example, (the original profile), Ir (roughness profile) and (wave profile) - the average length of a line segment used to identify inequalities characterizing the evaluate profile

- evaluation length In - the average length of a line segment used for profile evaluation,

- total traverse length It — the total length of a segment profile, as measured by the instrument [48].

PARAMETERS OF SURFACE A OF THE LAYER OF FUNCTIONAL PROPERTIES

The surfaces of the tiered functional properties devoted to ISO standard consists of three parts:

-Part 1 [PN-EN ISO 13565-1: 1999] applies filtering and general measurement conditions,

-Part 2 [PN-EN ISO 13565-2: 1999] defines the parameters determined from the linearization of the curve part of the material,

-Part 3 [PN-EN ISO 13565-3-2002] defines the parameters determined from the present cumulative distribution function of material participation on the mesh of the normal distribution.

Surfaces with tiered functional properties characterized with deep pits in the surface of a precisely machined surface layer. With this type of filtering a surface roughness typical filter occurs unwanted effects distorting profile.

Therefore a defined special two-step filtering procedure. In the first step of the primary profile there are deep recess cut in to the profile (at the average line obtained after filtration

Gaussian filter). The modified profile is re-filtered by the Gaussian filter to give an average line profile. After the "straightening" of the original profile based on the average roughness profile obtained line - Figure 13.

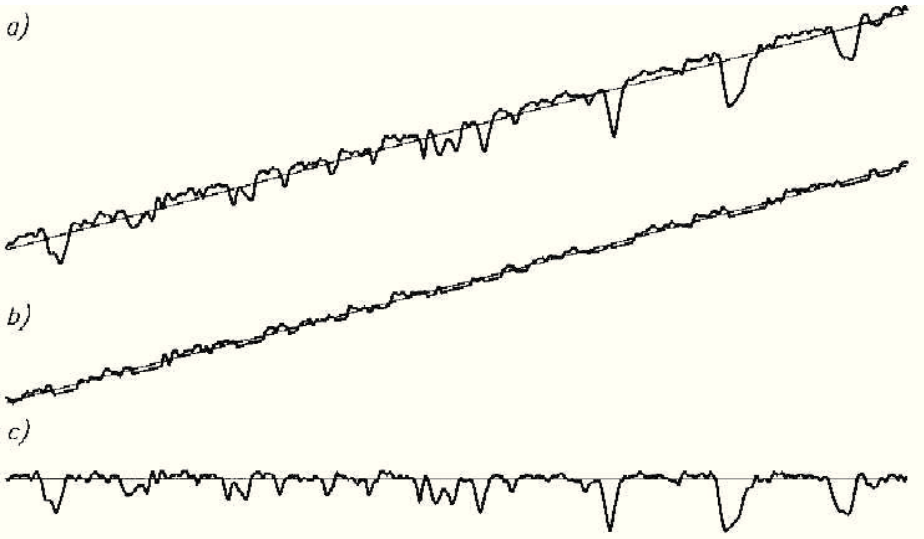

Fig.13 A filtering surface profile of layered functional properties according to EN ISO 13565-1:1999 a) the original profile of the applied line average achieved by first filtering, b) the line average profile of disapproved deep depressions, c) surface roughness profile [48]

Group parameters designated on the basis of material participation curve linearization (Fig.14):

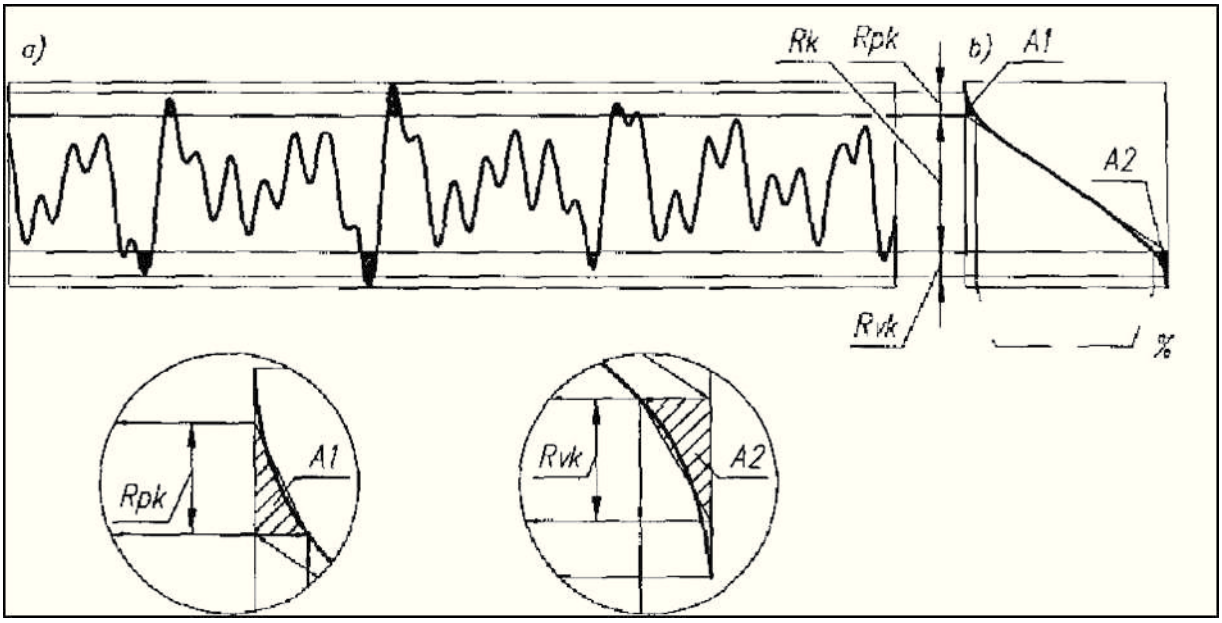

Fig.14 A figure for the definition of parameters: Rk, Rpk, Rvk, Mr1, Mr2, A1, A2[48]

- Rk — core roughness depth,
- Rpk — reduced peak height,

- Rvk — reduced valley,
- Mr1 — component relative to peaks — designated by the intersection of the line separating the protruding peak core profile roughness,
- Mr2 — material componentrelative to valleys — designated by the intersection of the line separating the deep recesses of the core, the roughness profile,
- A1 — reduced peak area,
- A2 — reduced valley area.

For the roughness core profile it means a roughness profile without distinctive hills and deep pits. The procedure to determine the above parameters is as follows. A simple linearization is determined for the central area of the curve.

Procedure to determine the above parameters is as follows. A simple linearization is determined for the central area of the curve part of the material, comprising of 40% of all the measured points profile. This area is located in the place where the secant includes 40% of the material which shows the smallest inclination (if there are several areas of the same inclination, then select the first one). Simple linearization is determined on the method of least squares. Parameters Rpk and Rvk calculated as the amount of surface right triangles equivalent surface, respectively the surface hills and surface pits. Similarly Mr1 parameters and Mr2 are the foundations of these triangles (Fig. 14) [43].

Advanced work on the stereometry surface description Nowicki [49, 50], Stout [51], Blunt [52].

In the simplest case the isometric image of the surface is achieved by the profilo-graphing at intervals of several to tens of micrometers. The obtained information can then describe the parameters or functions analogous to those previously discussed, but defined in three-dimensional space [43].

4 PREPARATION OF METALS UNDER GALVANIC COATING

4.1 Mechanical surface treatment

In order for galvanic coatings to have the required durability and aesthetics, it must be imposed on the smooth and clean surface physically protected metal. Because the surfaces of semi-manufactured goods are usually rough and heavily contaminated, they must be pre-prepared, with the most machining enabling:

enabling:

-removal of oxides and other impurities or defects in the surface layer, such as pitting, cracks, creases, scratches and stains;

-blunting and rounding of sharp edges, reducing the roughness and waviness of the surface;

- giving gloss or other decorative invoice (e.g. satin finishing) provided for the coating of surfaces galvanic

In the range of mechanical surface treatments there includes also a brightening and polishing of the galvanizing matt. Whilst using the mechanical treatment you cannot remove the shape errors in the objects.

As practice shows, modern manufacturing processes of participation mechanical surface treatment is not decreasing, despite the improvement of methods that cast of, forging, shaving treatment and already widely use the technology of obtaining shiny galvanic coatings in a bath.

The relative decrease in the mechanical of surface preparation balances the overall increase in the production of items covered galvanically, polished, and mechanically finishing the operation is continued to a considerable share in the costs of producing the products.

Observed whilst replacing the conventional grinding belt and polishing abrasive modern and less labor intensive methods such as machining and processing hydro-abrasive machining loose shaped bodies in containers. This applies especially to surface preparation with metal accessories that are mass-produced.

The development of modern methods that mechanically treat the surface, favors the use of galvanic baths with a capacity using a micro-smoothing final coating film, because the requirements for the output smoothness of the substrate in this case is not as high as for the substrate under the coating polished polishing. For the latter it is a rule - the possibility of brightening the applied coating is approximately equal to the initial brightening substrate prior

covering. Requirements concerning the surface roughness of the substrate for several types of galvanic coatings are presented in Table 2.

Table 2 The recommended surface roughness of metal objects before the imposition of galvanic coatings [53]

Type of coating	**Substrate**	**Surface roughness parameter [µm]**		**Comments**
		R_a	**R_z**	
Single-layer nickel technical	Steel	0,32 - 0,63	1,6 - 3,2	Glossy coatings obtained from the bath
Single-layer high gloss nickel	Steel	0,16 - 0,32	0,8 - 1,6	
Double-layer, nickel-chromium high gloss	CuZn, Steel	0,16 - 0,32	0,8 - 1,6	
A three-layer, copper-nickel-chromium high gloss	Steel	0,08 - 0,16	0,4 - 0,8	
	ZnAl	0,10 - 0,20	0,45 - 0,63	
Single-layer high-gloss zinc	Steel	0,32 - 0,8	1,6 - 3,8	
Single-layer protective zinc	Steel	1,25 - 2,0	7,5 - 6,3	
Technical chrome	Steel	0,16 - 0,32	0,8 - 1,6	
Single-layer nickel decorative polishing	Steel	0,04	0,2	

MECHANICAL TREATMENT SURFACE METHODS – ABRASIVE BELT GRINDING

It is a way of machining. The cutting tool is a belt, the surface of which is glued to an abrasive layer which is characterized by a much greater hardness than the material being processed. After becoming dulled of cutting edges abrasive in the outer layer, the belts are regenerated by removing the blunt parts and gluing a new layer of abrasive. A grinding belt is divided into:

1) disk - the belt is wound around a working disk,

2) disk-belt – the belt is wound onto two wheels, one of which is a disk working

3) The belt - the belt is wound on two wheels, a grinding process is performed on the linear part of the abrasive belt which is located on a special support called the wheel pin.

POLISHING ABRASIVE

It is called Polishing abrasive because of the smoothing treatment and the decreasing surface roughness resulting from the grinding which results in brightening. Polishing abrasive is analogous to the grinding belt, except that the roles of the tools met here are polishing

pastes applied to discs or belts. In contrast to the abrasive grinding contained in pastes may have a hardness less than the hardness of the processed material.

From previous studies the polishing abrasive process is not only caused by machining. The polishing abrasive performs an important role assigned to friction, the physical and chemical processes. This loosely embedded abrasive powder on a soft ground disc or belt polishing causing - in addition to machining - strong friction. As a result, heat is produced, which causes softening of vertices and their smudging irregularities. Next to micro-machining it is the second factor in the decrease of surface irregularities.

THE TREATMENT ABRASIVE BLASING

Abrasive blasting is a way of the treatment loosing the abrasive. The principle of this treatment lies in the fact that the stream of fluid (gas, liquid or gas-liquid) at a high speed are carried grains achieve such a high speed (about 100 m/s), that in spite of their small mass kinetic energy it is sufficient to perform the work machining.

The best known version of that is sandblasting treatment, which is used to clean the surface of castings, forgings and objects after heat treatment. Sandblasting took its name from the fact that it is used as an abrasive dry quartz sand. The importance of sandblasting is the result obtained in terms of surface roughness which are comparable with the results of the grinding grains numbered P36-50 now diminished to developing a treatment of hydro-abrasive.

During the dry machining a less smooth surface is usually achieved. It can be assumed that the machined surfaces will be characterized by similar parameters of roughness, if dry machining applies the abrasive grains less than two numbers in the hydro-abrasive treatment.

Recent research shows that the use in the treatment of dry abrasive spheres (with a diameter of 0,1 mm) allows you to obtain the production conditions corresponding to the normal polishing effect ($Rz \approx 1$ μm).

TREATMENT OF LOOSE SHAPED BODIES

Treatment consists of loose fittings or plastic shear deformation (crushed) drop roughness and waviness of objects on the surface which is arranged together with the shaped bodies and wetting solution in a container planisher, propelled into a rotary motion, oscillating or rotary-oscillating. The effects of the treatment with the participation of loose shaped bodies of ceramic are comparable with the results of rough grinding [53-73].

4.2 Physico-chemical treatment of surfaces

Cleaning the substrate surface prior to the deposition of galvanic coatings involves the removal of the mechanical impurities, oils, fats, and their derivatives, corrosion products and other contamination accumulated during the production process.

Mechanical contamination is the reminiscent of the mechanical treatment object (milling, grinding, etc.), and is generally quite easy to remove, because the adhesion is determined by the viscosity of lubricants, which are usually wetted. The exception is the presence of graphite a drag operation, which pounds into cracks and crevices that are difficult to remove by both mechanically and chemically methods.

The traditional process of preparing the surface before the deposition of galvanic coatings typically consists of the following operations:

1) preliminary degreasing,
2) digestion,
3) rinsing the cold,
4) chemical degreasing,
5) rinsing hot and cold,
6) electrochemical degreasing,
7) rinsing hot and cold,
8) activation,
9) rinsing the cold.

This is the minimum required of the operation of which basically in any case, does not resign. Where necessary you can repeat the individual operations or turn to them other methods (such as degreasing of simultaneous action of ultrasound).

4.2.1 Purification by ultrasound

Vibrations of high frequency (>20 kHz) give rise to periodic densities and rarefaction solution contained in the scrubber. Rarefication of the solution may cause a complete disruption in places where the liquid is to form a hollow space point (cavitation). Following the strong rarefaction of liquid, its rapid density triggers the formation of a "wave of high pressure."

Using the ultrasonic method, you can obtain a degree of purification unreachable sometimes other methods - especially when you have components with small sizes, like

transistors, parts for watches, radio lamp etc., or a part of a strongly profiled, the clean-up time is very short, and the consumption of small wipers.

4.2.2 Pickling

PICKLING OF STEEL AND CAST IRON

Pickling steel and cast iron is carried out in hydrochloric acid or sulphuric acid (VI) or without using the inhibitor at ambient temperature or elevated temperature in the case of H_2SO_4. Pickling generally occurs quickly. It is more resistant to corrosion products or the constant, a content more than 5% of dopants require special pickling. Sometimes softening enough scalings in molten NaOH with the addition of oxidizers or reducing agents. After this operation it is out more easily under the influence of both mechanical factors and chemical. This method is highly cost effective in the mass production of products (for example directly in the steel works).

In Poland, purification of the molten NaOH is not prevalent, a more resistant contamination is typically removed by digestion in a properly selected mixture of acids.

Often a electrochemical digestion is used. It involves more intensive dissolution of a projecting parts surface. The most frequently used 5-40 percent H_2SO_4. The electrodes are in the form of leaden or graphite plates.

The ease of steel and cast iron hydriding forces the anodic pickling, which in turn may cause an over pickling surface. Pickling iron is harder than steel pickling. It should be done in the shortest possible time necessary to prevent the discovery of carbon and silica dissolved in the iron.

Documents of cited literature from the sixties is a fundamental documentation, as the same preparatory processes have no significant changes. Changes in the methods of purification are little or not followed at all. The proportions in the use of methods based the on purification in the aqueous solutions (approximately 65%), these methods based on the use of chlorinated hydrocarbons (about 25%) and other (5%), for many years with low volatility. Slightly larger changes are observed while the devices are used [74-83].

5 GENERAL CHARACTERISTICS OF THE PROCESS OF ELECTROLYTIC DEPOSITION OF METALS AND THE IMPORTANCE OF PROPER SELECTION OF COATINGS

An application of electrolytic processes for metals should be then, when it comes to getting the clear coating, single or multilayer, rather small and usually not exceeding a thicknesses regulated exactly by tens of micrometers, for relatively small areas.

A proper selection of the coating determines the possibility of imposing it at the lowest cost of production, while ensuring the required quality of the surface covered and predicted useful life products.

Properly selected and properly made galvanic coating contributes to the overall improvement of the quality of the products, their proper and reliable operation and to prolong the time of their use.

The most important benefits arising from the use of electrolytic metal deposition methods in comparison with other methods are:

1) the uniformity of a large coating obtained,
2) the possibility of obtaining the desired thickness of coatings (in a relatively wide range),
3) a low temperature bath (not exceeding the boiling point of water),
4) relatively small porosity derived coatings,
5) high fineness imposed coatings,
6) the possibility of strict control of deposition process,
7) a small loss of embedding metal,
8) the ability to embed many metals and alloys as coatings single-and multilayered,
9) the possibility of obtaining different coatings and applications of different corrosion resistance suitable for the environment in which they are to be used,
10) a good adhesion of coatings,
11) high speed coating,
12) the ability to automate the process of [84].

CLASSIFICATION OF GALVANIC COATINGS, DEPENDING ON THEIR DESTINATION

Shell applied in practice can be divided into the following groups:

1) protective coatings - with the task solely to protect the base metal from corrosion,

2) decorative coatings - applied to improve the surface appearance (color, gloss, smoothness),

3) protective, decorative coatings – used as a protection against corrosion and put into effect at the same time preserving the decorative metal surface properties of substrate,

4) shell (functional)-used in order to obtain certain physical properties of the surface or technological, for example. increased resistance to abrasion, changing the coefficient of friction, to improve the electrical properties of the surface, to improve the ability of connecting by soldering, changing dimensions covered parts, used, surface regeneration increased the degree of reflection and luster surface, the security referred to in other surface treatment processes at run-time and getting thick layers in galvanoplasty.

Classification from the point of view of the protection mechanism of metal substrate for coating:

1) anodic coating - made of metal, which within a specified corrosive environment has the potential which is lower than the potential of the base metal and, therefore, not only isolates it from the surrounding environment, but also protects it electrochemically, succumbing to alone to corrosion, in case of leaks and the formation of electrochemical cell corrosion of the metal coating is (e.g. zinc coating on steel),

2) cathodic coating - made of metal, which within a specified corrosive environment has a higher electrochemical potential of the base metal potential, and thus protects the surface of the isolation from the surrounding environment, and in the case of leaks and the creation electrochemical cell corrosion of the substrate is metal (e.g. nickel coating on steel).

Scheme corrosion coating anode and cathode are shown in Figure 15.

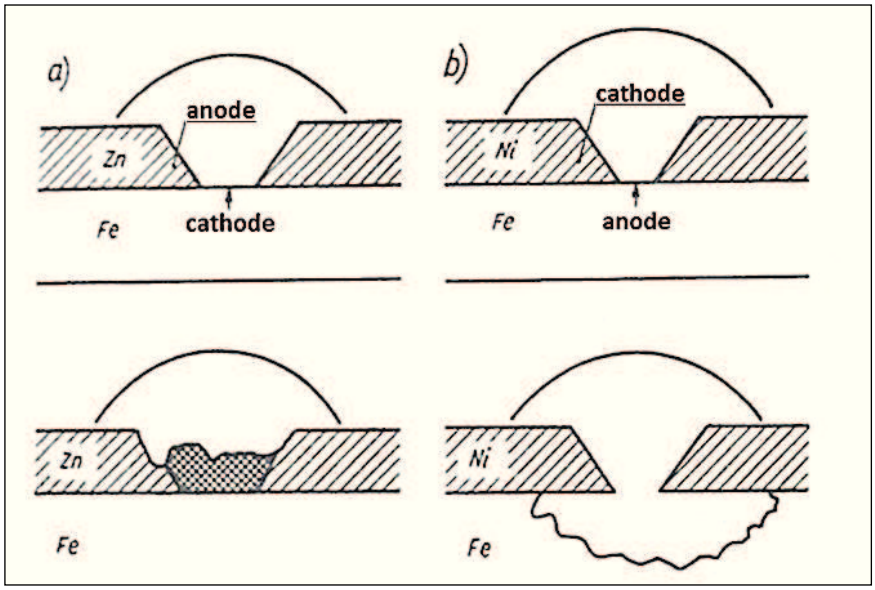

Fig.15 Scheme corrosion coatings: a) the anode, b) the cathode [53]

A classification from the perspective use of the goods covered coatings according to PN-H-04652: 1973 [85].

1) coatings used in corrosive environments very light B
2) coatings used in corrosive environments light L,
3) coatings used under mild environments U,
4) coatings used in heavy conditions, C,
5) coatings used in extremely heavy conditions W.

The standard PN-H-04652: 1973, despite being withdrawn and replaced by PN-EN 1403:2002, it is still however often found in the industry.

Determination of the conditions of use, according to PN-EN 1403:2002 specifies conditions in which the coating should be resistant to the effects of the atmosphere in which it is intended to be used. Determination terms of the use of corresponds to one or more specified types of atmospheres in European standards for each of the coatings.

Examples of designations conditions used and the corresponding description of the conditions of use are given in Table 3.

Table 3 Examples of conditions use of coatings according to PN-EN 1403: 2002

Determination conditions of use	Description of the conditions of use
0	Used for decorative purposes only
1	Used inside the atmospheres where it is warm and dry
2	Used in inside areas where condensation may appear
3	Used outdoors in moderate conditions
4	Used outdoors in conditions of strong corrosive effects, for example marine or industrial

5.1 Copper plating

The copper plating is used for protective and decorative purposes. Copper is most often used as one of the layers of the multilayer coating copper-nickel-chrome, it also has technical purposes [86-88].

Electroplated embedded copper is used in electroforming and also as a protection of certain surfaces of the steel during carburizing diffusion.

Cu coatings are porous, so they are used mostly as a sub-layer imposed on steel underneath nickel or chrome. Uses a good adhesion of the coating Cu, which is of decisive importance for the quality of decorative coatings. The thickness of the coatings Cu chosen depending on the destination. The protective-decorative coatings type Cu-Ni-Cr sub-layer thickness of Cu is about 0,01 ÷ 0, 025 mm.

For copper plating there are two basic types of baths - alkaline and acidic. Among the alkaline baths there are usually cyanide baths or pyro-phosphatizing which are used.

It also applies to copper plating baths with gloss, containing the same components as bath fast efficient, but often in a different ratio with various kinds of additives brightening and wetting substances [89].

Among the copper plating bath of acid found in practical use, only the sulphate baths, and (to a lesser extent) baths fluoroborates [90].

5.2 Nickel plating

Nickel coatings should apply not only as a protective coating against corrosion and as a decorative coating, but also as a hardening coating for soft metals and alloys. They are used in the industries: automotive, sanitary and surgical, optical, food, printing, home use products, and fancy goods-decorative. Nickel coating for iron is a cathodic coating and rather mechanically protect, i.e., that the coating does not contain pores. On a steel substrate, a nickel layer underneath is often applied to the copper layer.

To achieve the lowest porosity, apply nickel layers to thickness, of about 20-30μm, which significantly increases the cost of the coating.

Nickel can also absorb relatively large quantities of hydrogen, which is often the reason for the quality of the coating being poor [85].

Nickel layers formed on the cathode by electrolytic dissociation of a corresponding salt of nickel. For example, nickel sulphate - $NiSO_4$ disintegrates into ions Ni in solution and acid the rest SO_4 by the reaction:

$$NiSO_4\ Ni^{++} + SO_4^{--}$$

During the electrolysis nickel is transferred from the anode to the cathode, i.e. the dissolution of the nickel anode and nickel deposition on the cathode, and the electrolyte is the only ion transporting medium.

Proper nickel plating process depends primarily on maintaining proper pH, temperature and current density.

As the basic salts incorporated in a nickel of electrolytes is mainly used:

-nickel sulfate, $NiSO_4 \cdot 7H_20$

-nickel sulfate-ammonium $NiSO_4 (NH_4)_2 \cdot 6H_20$

-nickel chloride $NiCl2 \cdot 6H_20$,

-chlorides and fluorides of alkali elements (in order to increase the electrical conductivity of the electrolyte).

The most popular bath to apply decorative coatings, undergoing pre-polishing, is the Watts bath containing:

- nickel sulfate $NiSO_4 \cdot 7H_20$, - 240 g/dm^3
- nickel chloride $NiCl_2 \cdot 6H_20$ - 20 g/dm^3
- boric acid H_3B0_3 - 25 g/dm^3

The process takes place in conditions of:

- pH - 2 ÷ 2,5

- temperature - 45°C
- current density - 3÷5 A/dm^2

Currently, electrolytes is widely used for the preparation of glossy nickel coatings. These coatings have a mirror, glossy surface and are sufficiently resistant to weathering [79, 85, 91, 92].

5.3 Chrome plating

Chrome plating is the most well-known and universally used process for applying a protective coating for the electrolytic method. Chromium plating process is the technically difficult and quite energy intensive. It is characterized by a relatively low current capacity (efficiency).

Current capacity is determined by the percentage of the ratio of the mass of metal at the cathode separated by electrolysis, under specified conditions to the mass calculated from Faraday's first rights. Also the large so-called current density is required, the current through the electrolyte per unit area of the cathode.

The chromium plating is also characterized by a low throwing power of electrolyte - the plating bath. Throwing power bath has a tendency towards the formation of a uniform plating layer on the cathode surface. Despite these unfavourable parameters chromium plating is widely used because of the performance on your valuable chromium coatings. Chrome plating is a plating baths lined with rubber or chemical-resistant Winidur - hard polyvinyl chloride, supplied with DC current from the rectifier or DC generator.

An aqueous solution of chromic acid anhydride with the addition of sulfuric acid is used for chromium plating baths. Depending on the composition it can be distinguished into three types of baths: diluted, concentrated and universal (Table 4).

Table 4 Baths used for chrome plating

Bath	**The composition of the bath [g/dm^3]**	
	CrO_3	H_2SO_4
Diluted	150	15,0
Universal	250	2,5
Concentrated	350	3,5

For chrome plating baths based on chromium compounds on the sixth degree of oxidation - chromic acid (VI) - are extremely dangerous to the health of humans, animals and the environment. For this reason, they are provided over the years for the intensive work on the replacement of chromium plating in the process of chromium (VI) compounds of chromium on the third degree of oxidation.

Work from this scope, conducted in Poland led to the development bath containing chromium chloride (III).

The bath is a patented; is it a good quality chromium coating with a thickness of up to 2 μm [93] This chrome coating thickness is sufficient for decorative coatings.

Chromium iron alloys depending on the construction coatings and their production technologies can be classified into decorative and technical. Decorative chromium coating is applied to the sub-layers of copper and nickel or nickel. The role of the outer layer of chromium thickness 0,3 ÷ 5,0 microns consists only to protect the surface from scratches and fogging. The requirements as to the quality of coatings are specified in PN-EN ISO 1456:2009. For decorative, chromium plating bath are used in a self-directed or concentrated at 47 °C with a current density in the range 20 to 35 A/dm^2. The technical chromium plating is applied as a coating to a thickness of 1mm - directly to steel or copper alloys in order to obtain a suitable hardness and resistance to abrasion.

During the chromium plating emitting hydrogen on the cathode substrate is diffused into the material and this causes hydrogen embrittlement. To remove the effects of this phenomenon it often takes the dehydrogenation process It consists of the elements held at a temperature of 177 ÷ 197 °C in air circuit for a minimum of 2 hours. Chromium coating can be gray, glossy or milk, depending on the manufacturing conditions. The best quality glossy chrome coatings have a hardness of 1000 ÷ 1200 HV (Fig. 16).

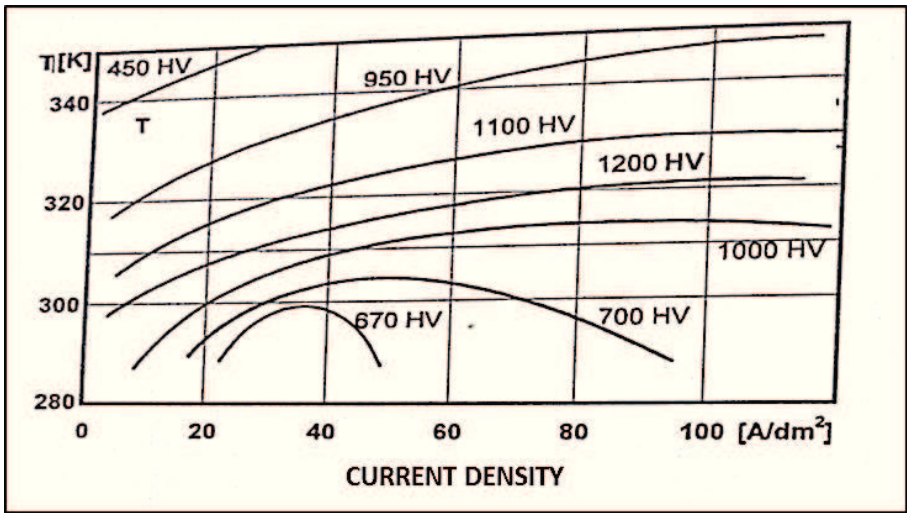

Fig.16 An influence of the process parameters on the hardness of chromium plating [94]

The coatings do not change their appearance in air and are resistant to the action of nitric acid and sulfuric acid and to frictional wear. The outer layer of chromium has a thickness of more than 1.5 um in the multilayer coating it is a sealed decorative, abrasion resistant and protects the substrate against corrosion.

Decorative coatings for Cu and Ni the sub-layer is commonly used in the manufacture of components for cars, motorcycles, bicycles, wagons and trams, sanitary fittings, furniture and a construction of fittings, precision instruments and other decorative elements that need to have a finished look, be resistant to abrasion and corrosion.

Technical chromium coatings are more porous. Their tightness and resistance to corrosion protected substrate is achieved only at thicknesses greater than 0,1 mm.

Technical chromium plating applies to both new and regenerated objects. The coatings are smooth, chemically resistant, hard and low-friction in combination with both the surface of the chrome as well the steel [79, 94-98].

6 THE PURPOSE AND SCOPE OF WORK

The purpose of this scientific paper is to analyse the surface layer steel DC01 depending on the corrosion resistance and adhesion of metal coatings on medical equipment. The assumption is looking at the choice of metallic coating, which when used for the best medical equipment will protect them from corrosion.

To assess the preparation of galvanic coatings type nickel-chromium, nickel-nickel-chromium, nickel-copper and copper without a sub-layer being imposed electrolytically, will determine the nature of the changes in the corrosion and structural steel DC01 used as a construction material in the production of medical equipment.

For testing corrosion resistance corrosive fluids are selected: Ringer's solution, artificial blood (SBF) and a solution of artificial saliva. These are the solutions, which are most commonly encountered when in contact with the protective coatings medical equipment such as operating tables, surgical, rehabilitation beds and bedside cabinets.

A methodology - the work plan of the doctoral dissertation:

- analysis of a research object,
- predict the research material,
- preparation of test samples (grinding, polishing) and the method of marking,
- assessment the geometric structure of the surface before applying galvanic coatings,
- electroplating imposition of metallic coatings (Ni, Cr, Cu) in the research material,
- an assessment of the surface layer of metallic coatings,
- metallographic research,
- X-ray microanalysis,
- research potentiodynamic corrosion resistance of metallic coatings.

7 RESEARCH METHODOLOGY

➢ **Research object analysis**

- the topography of the surface layer in terms of three-dimensional objects
- the quantitative and qualitative analysis of the chemical composition of DC01 steel was carried according to PN-EN 10130:2009
- measurement of hardness using a universal hardness meter Zwick / Roell ZHU-250 according to PN-EN ISO 6507-1:2007
- the microstructure of steel DC01 – part of the ear of the railing Fig. 24 rehabilitation bed
- a microscopic measurement of coating thickness
- X-ray microanalysis steel element ear cut of a side railing electron microprobe model JEOL JXA-733
- bacterial tests on the corroded construction element of rehabilitation beds

➢ **Experimental materials**

- steel DC01 cold rolled in the form steel sheet size 1000mm x 2000 mm and a thickness of 3mm - the construction elements of medical equipment,
- stainless RSt37-2 NBK profile Ø28x2,5x1800 mm tube (welded, cold-drawn) - the construction elements of medical equipment

➢ **Types of experimental coating systems**

- nickel-nickel-chromium - Fe//Ni20d/Cr - electrolytical metallic coatings, nickel coating double layer called duplex, mostly metallic coating used to protect medical equipment
- nickel-chromium - Fe//Ni10b/Crr - electrolytic metallic coatings, single-layer coating of nickel
- nickel-copper - Fe//Ni3s/Cub - electrolytic metallic coatings, semi-gloss nickel-layer coating, gloss copper
- copper - Fe//Cus - electrolytic metallic coatings, copper matte without sub-layer

- **Application of coating systems**

- electrochemical metallic coatings using a standard electroplating bath

- **Tests on experimental substrate materials**

- research and analysis of the chemical composition of the material to predict quantitative and qualitative for steel DC01 and RSt37-2 NBK according to PN-EN 10130: 2009
- measurement of the substrate hardness of the steel according to PN-EN ISO 6507-1:2007
- microscopic analysis of the structure of steel samples on the disk and the tube profile according to PN-EN ISO 643:2005
- 3D geometric structure - steel substrate according to PN-EN ISO 4287:1999 and BS EN ISO 13565-2:1999
- X-ray microanalysis point of the chemical composition of the steel substrate

- **Testing of the metallic coatings**

- electrochemically applying metallic coatings according to the guidelines of the PN-EN ISO 1456:2009 and BS EN 1403:2002
- roughness of the surface layer of the metallic coatings according to PN-EN ISO 4287:1999 and PN-EN ISO 13565-2:1999
- measurement thickness coatings and adhesion to the metallic substrate
- X-ray microanalysis point of the chemical composition of the coatings by electron microprobe JEOL model JXA-733
- potentiodynamic testing the corrosion resistance of metallic coatings in body fluids

8 A DESCRIPTION OF STUDIES CONDUCTED RESEARCH OBJECT ANALYSIS

8.1 Research object analysis

The object of the conducted research a was rehabilitation bed side rail which had visible corrosion, subjected to systematic disinfection in a disinfection chamber to maintain the sterility of medical devices (Fig.17 a, b, c). Locus, the area subjected to corrosion is difficult to access - the inner part of the ear side rails (Fig.17b).

The selected object study stages are presented below:

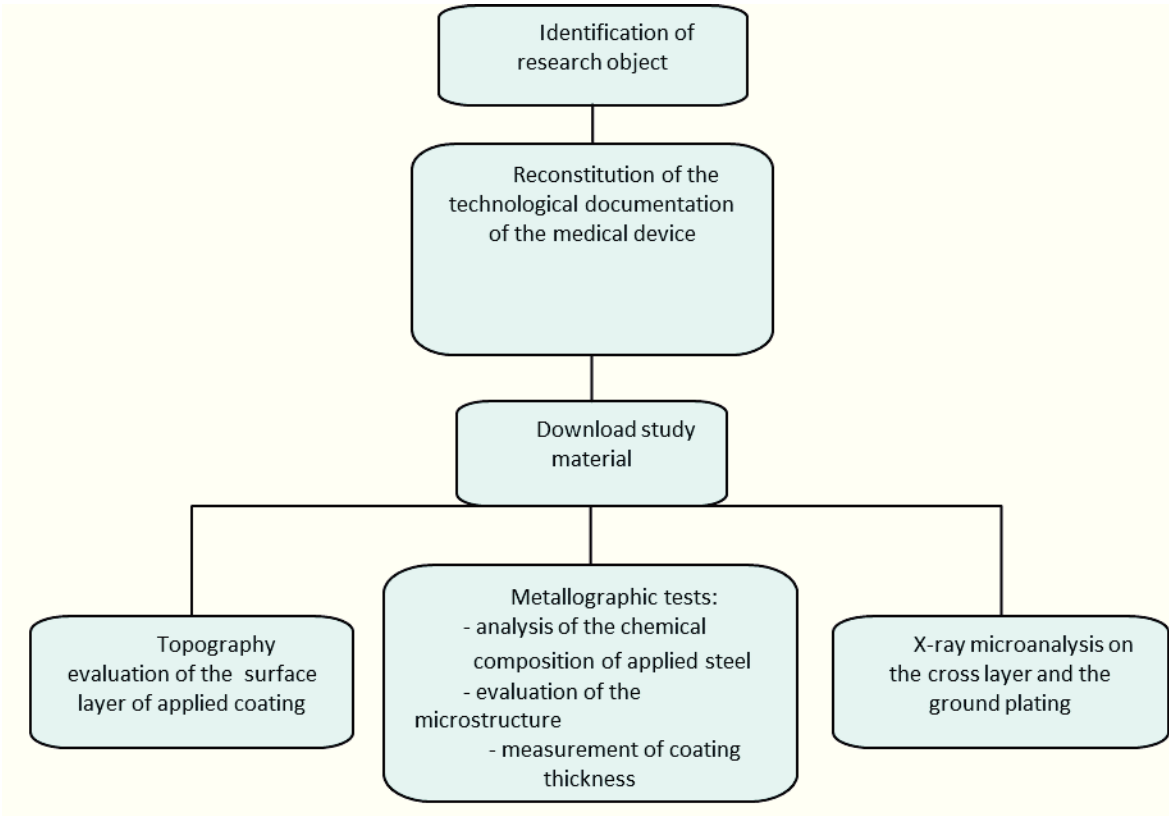

Figure 17c the detailed research object was the ear, the side rails PB-02.1/N-359/00 - year 2000).

Fig.17 a) Rehabilitation bed, equipped with side rails PB-02.1/N-359/00 - year 2000, b) place of the corrosion, c) a side rails data plate symbol LR-01.1/N-374/00 [own investigations]

Technological documentation of the side rails marked as PB-02.1/N-359/00 includes information that to ear production construction material - stainless steel cold-rolled DC01w was used with a 3mm thickness and the information about the technology course of the ear preparation for galvanic treatment.

Topography measurements were made on the surface layer, cut out from the part of the side rails ear without any visible corrosion (Fig. 18). A three-dimensional graphical image with measurement results is presented at Fig. 19.

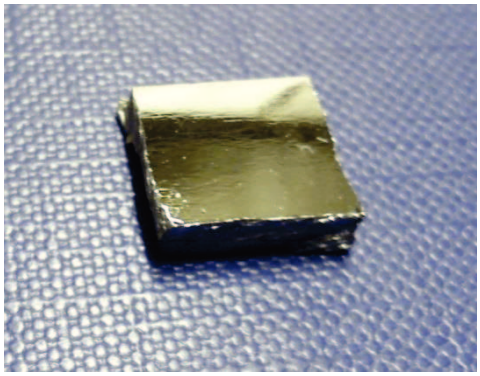

Fig.18 The part cut out of a side rail with no corrosion traces PB-02.1/N-359/00 [own investigations]

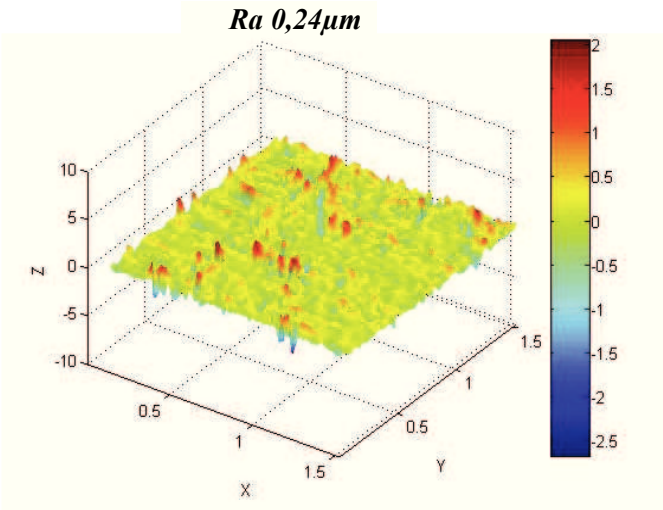

Fig.19 The topography of the surface layer in terms of three-dimensional

The quantitative and qualitative analysis of the chemical composition of DC01 steel was carried according to PN-EN 10130:2009 the standard emission spectrometer with an inductively coupled plasma ICP-OES. Whereas, carbon and sulfur were determined with a carbon and sulfur analyzer LECO CS-125. The results are presented in Table 5.

Table 5 The steels for testing according to EN 10130:2009 and the results of chemical analysis

Results source	**DC01 chemical analysis in [%] by weight**									
	C	P	S	Mn	Al.	Si	Cu	Cr	Ni	Fe
Accoring to PN-EN 10130:2009	≤ 0,120	≤ 0,045	≤ 0,045	≤ 0,600	-	-	-	-	-	rest
According to chemical analysis	0,082	0,036	0,040	0,520	0,028	0,046	0,049	0,009	0,031	rest

A hardness measurement was performed using a universal hardness tester Zwick / Roell ZHU-250, PN-EN ISO 6507-1:2007. The average hardness was 106 HV1.

A microscopic analysis of the element cut from the ear at a magnification of 100, 500 and 1000x indicates that the steel structure is composed of fine grain typical of cold-rolled products (Fig. 20).

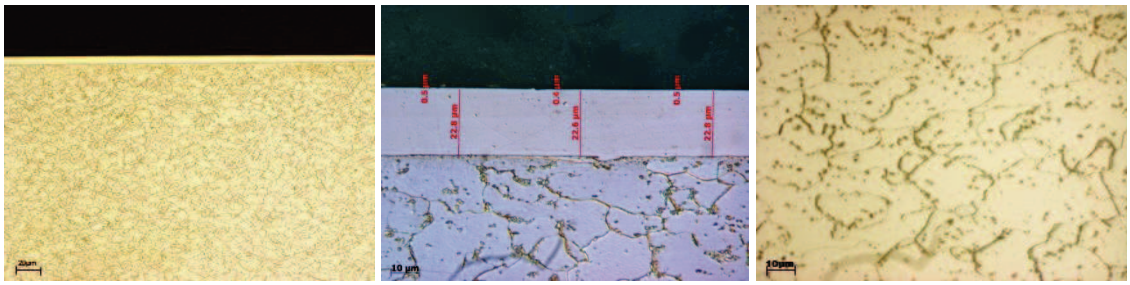

Fig.20 The microstructure of steel DC01 – a fragment of the ear of the railing, ***a)*** *magnification 100x,* ***b)*** *magnification e 500x,* ***c)*** *magnification 1000x*

A microscopic measurement of coating thickness were performed using a microscope metallographic Carl Zeiss AxioImager.M1m at a magnification of 500 and 1000x.

An x-ray microanalysis of the ear element cut from the side railing steel was made by an electron microprobe JEOL model JXA-733 application.

The sample cross sections with protective coating with corrosion (Fig.22) and without corrosion (Fig.21) were analyzed metallographically.

The analysis was conducted at an accelerating voltage of 15kV. The analysis results of the examined metallographic specimens cross sections are presented in Table 6.

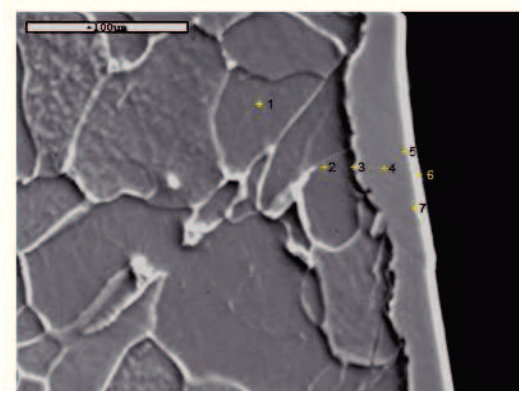

Fig.21 An x-ray point microanalysis on the cross section

Table 6 The results of the chemical microanalysis to cross the boundary layers of nickel-nickel-chromium of the background and of the material (ear cutting from a side rails without corrosion)

Analyzed element	Place analysis						
	1	2	3	4	5	6	7
	Content in [%] by weight						
Fe	98,90	99,76	98,83	99,80	99,84	2,2	4,88
Ni	0,19	0,13	0,16	0,17	0,79	94,46	94,02
Cr	0,00	0,00	0,00	0,01	0,02	3,96	3,16

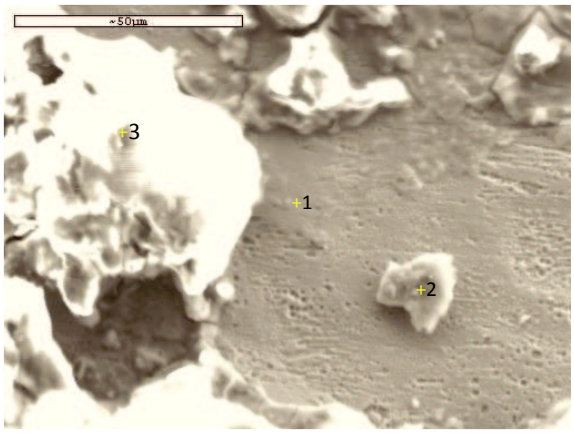

Fig.22 An x-ray microanalysis point corrosion products

The graphs X-ray energy spectra of the sample with corrosion - EDS (Energy Dispersive Spectroscopy) – Fig. 23.

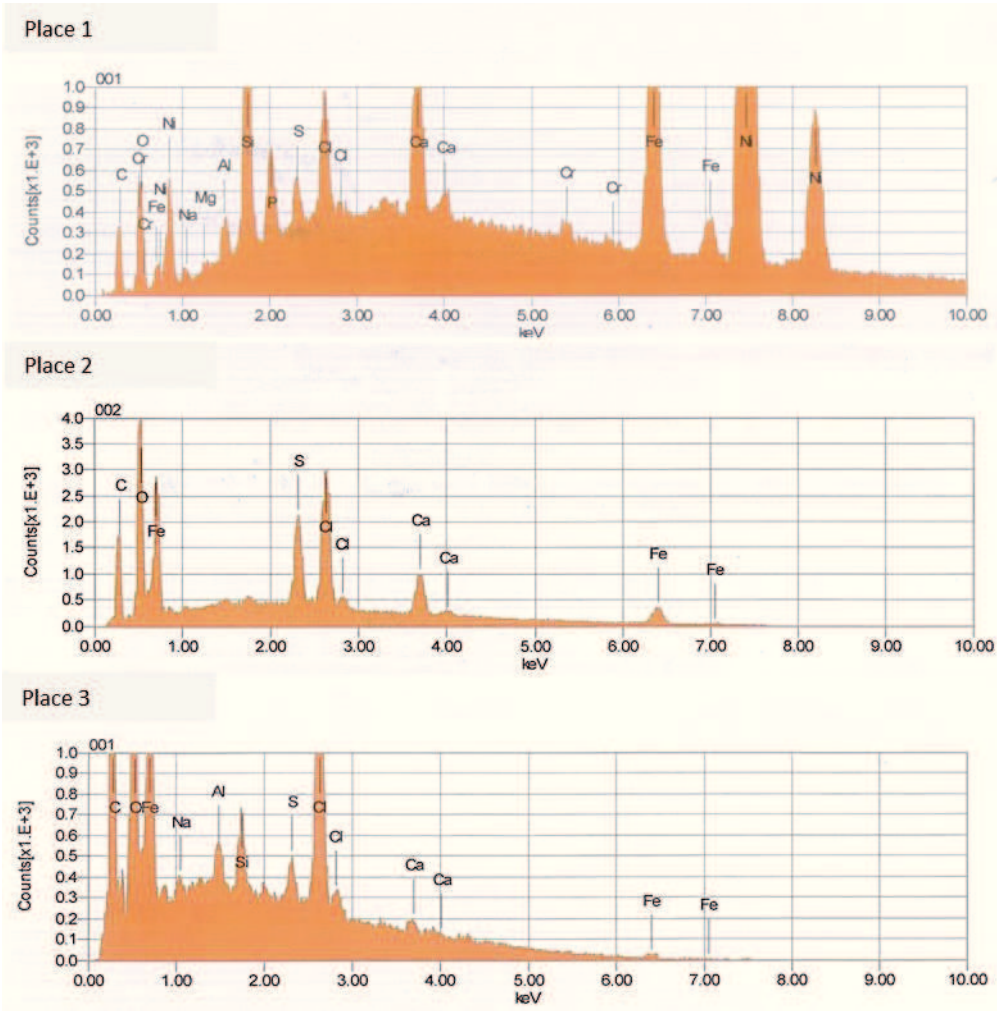

Fig.23 EDS corrosion products element cut side handrail construction

8.2 Bacteria identification at corroded construction's elements surface

For testing, the medical equipment - rehabilitation bed marked as LP-01.0 (production year - 1994) was chosen, where the local corrosion was observed. Next, two elements with visible corrosion were cut from the steel construction of the bed (Fig. 24). This material with galvanic coating type nickel-nickel-chromium was subjected to microbiological examinations in order to establish the bacteria kind settling in niches, cavities and on a protective layer of examined elements.

Samples were incubated in 37 °C in 50 BHI ml. Every hour bacterial culture was mixed within 5 min, and the surface inoculation was being carried out on BHI agar: after the first hour 0,5 ml, in next following hours 0,1 ml. After 24 hours of incubation the bacterial cultures were identified and counted. After 24 hours of cultivation 0,1ml of every fluid culture in dilution 10-4 and 10-6 was surface inoculated on a chosen basis. The final bacteria identification of the biochemical API tests were made.

At the first sample(Fig. 24 b) Bacillus cereus strain was identified, whereas on the second (Fig. 24 c) Staphylococcus aureus and Acinetobacter baumani were identified.

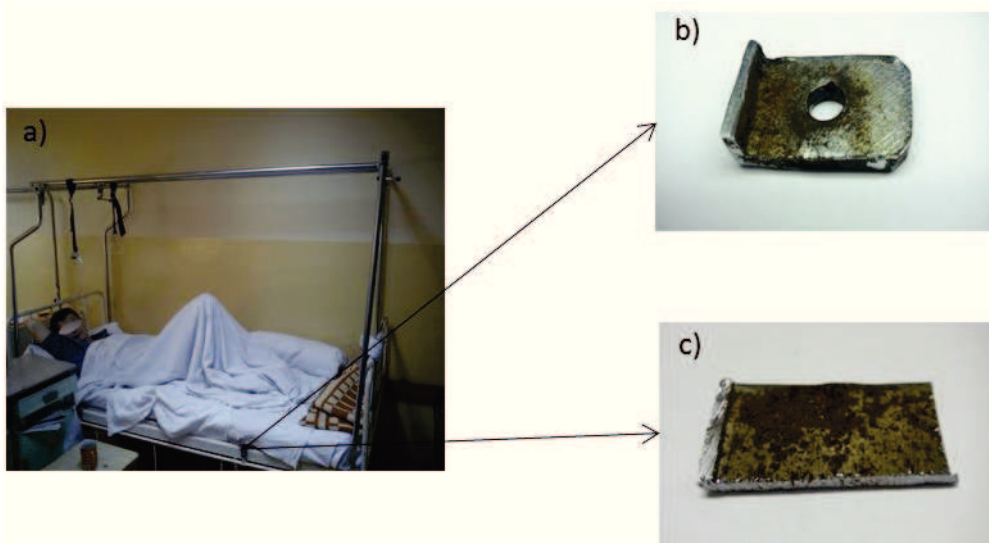

Fig.24 A rehabilitation bed with corrosion centers [own investigations]

8.3 Material for research

For testing the chosen construction material - in the form of steel DC01 cold rolled steel sheet size 1000mm x 2000 mm and a thickness of 3mm (Fig. 25 a, b, c) and stainless RSt37-2 NBK profile Ø28x2,5x1800 mm tube (welded, cold-drawn) (Fig. 27) for the construction elements of medical equipment.

With randomly selected areas of cut sheet sample (with a diameter of 14,6 mm and technological hole Ø1,5 mm at a distance of 1 mm from the lateral edge of the disc – Fig.26) Laser BYSTRONIC - model Byspeed 3015.

However from the pipe there were samples prepared for 50 mm lengths with the technological hole technology at Ø3, 5 mm, 5 mm distance from the side edge (Fig. 28).

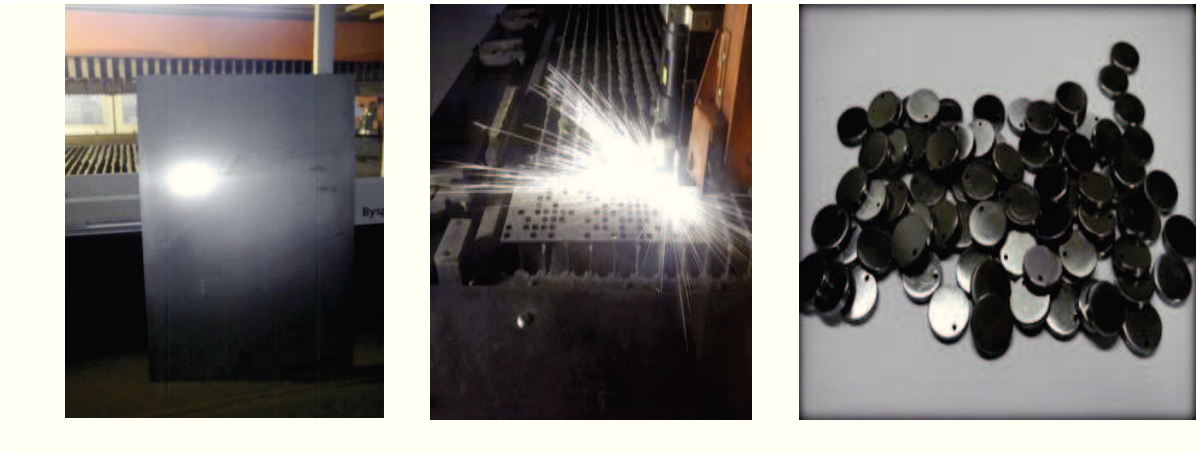

Fig.25 Material for testing, a) steel sheet-steel DC01, b) way to cut outs samples, c) prepared samples [own investigations]

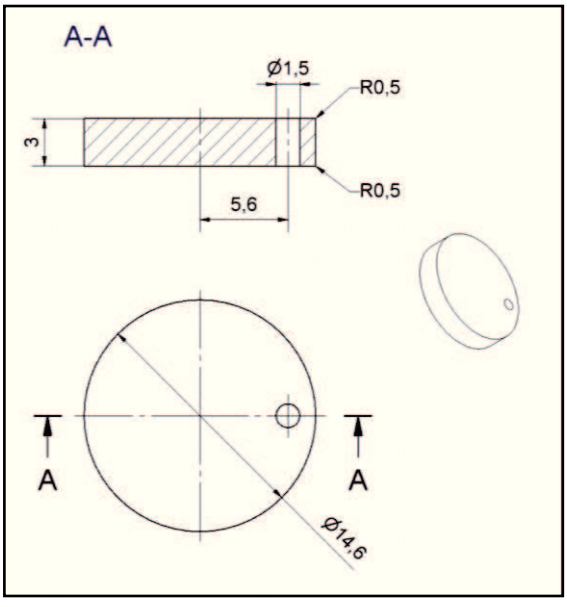

Fig.26 Figure the sample in the form of a steel disc

Fig.27 Steel - species RSt37-2 NBK designated to research – a general view [own investigations]

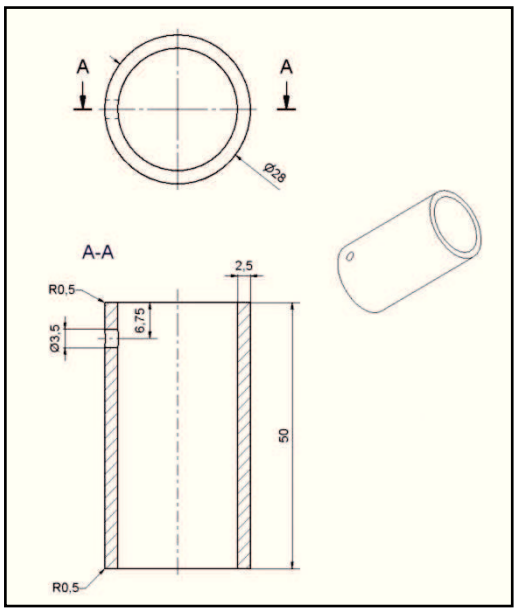

Fig.28 Figure steel sample tube geometry

THE CHEMICAL COMPOSITION OF THE BASE MATERIAL

The quantitative and qualitative analysis of the chemical composition of DC01 and steel was carried out according to PN-EN 10130:2009 a standard emission spectrometer with inductively coupled plasma ICP-OES. Whereas, carbon and sulfur were determined on the carbon and sulfur analyzer LECO CS-125. The results are presented in Table 7.

Table 7 Steels for testing according to EN 10130:2009 and the results of chemical analysis

Results source	**The chemical composition of steel DC01 in [%] by weight**									
	C	P	S	Mn	Al	Si	Cu	Cr	Ni	Fe
According to PN-EN 10130:2009	≤ 0,120	≤ 0,045	≤ 0,045	≤ 0,600	-	-	-	-	-	rest
According to chemical analysis	0,070	0,020	0,016	0,490	0,034	0,060	0,056	0,013	0,032	rest
Results source	**The chemical composition of steel RSt37-2 NBK in [%] by weight**									
	C	P	S	Mn	Al	Si	Cu	Cr	Ni	Fe
According to PN-EN **10130:2009**	0,09÷0,15	≤ 0,040	≤ 0,040	0,35÷0,60	≤0,07	≤0,05	-	-	-	rest
According to chemical analysis	0,14	0,010	0,006	0,42	0,042	<0,02	-	-	-	rest

8.4 Preparation of samples for research

Samples of steel in the form of discs (Fig. 15), mechanically grinded abrasive disks with granulation 80 and 120 with a grinding paste of ABRA applied then polished.

However, the geometry of the sample tube on the grinded abrasive disks with granulation 240, 400, 600, 800 without polishing (Fig.29).

The sample preparation was compatible with the technology to prepare the construction elements for the galvanic machining in the production of medical equipment.

MARKING OF MATERIAL RESEARCH

Giving the individual characteristics of samples were made and the information on how to marking are included in Table 8**.**

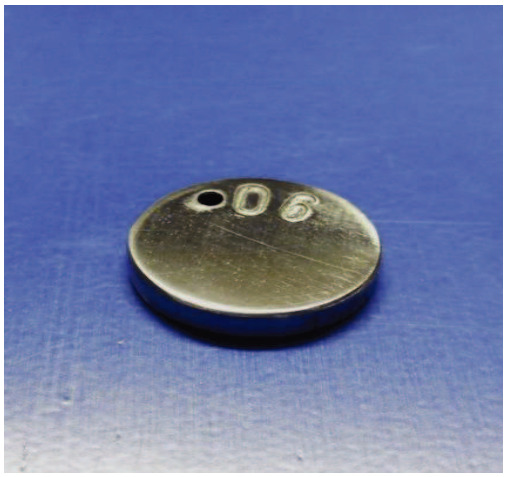

Fig.29 The sample steel geometry disc with a feature No. 06

Samples of pipe profile labeled similarly. An example of a way to mark is found in Figure 30.

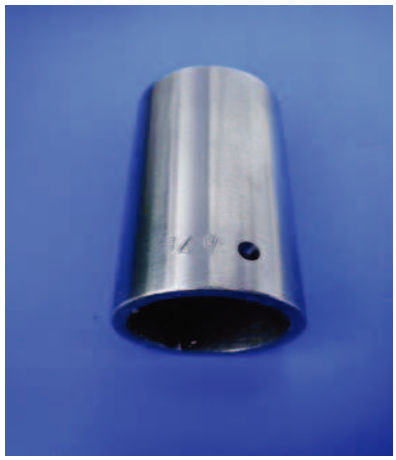

Fig.30 The sample steel pipe geometry with feature No. R78

Table 8 A method of labeling the samples

Groups of samples	**Identification of flat samples Ø14,6 mm**									
0	01	02	03	04	05	06	07	08	09	010
A	11	12	13	14	15	16	17	18	19	110
B	21	22	23	24	25	26	27	28	29	210
C	31	32	33	34	35	36	37	38	39	310
D	71	72	73	74	75	76	77	78	79	710
Groups of samples	**Identification of samples from the pipe Ø28x2,5x50 mm**									
R0	R01	R02	R03	R04	R05	R06	R07	R08	R09	R010
I	R11	R12	R13	R14	R15	R16	R17	R18	R19	R110
II	R21	R22	R23	R24	R25	R26	R27	R28	R29	R210
III	R31	R32	R33	R34	R35	R36	R37	R38	R39	R310
IV	R71	R72	R73	R74	R75	R76	R77	R78	R79	R710

8.5 An assessment of the geometric structure surface of samples before and after the application of metallic coatings

The study of the surface layer of the disc profile samples (Ø14, 6 mm) and samples from the pipe Ø28x2,5x50 mm before (after grinding and polishing), and after putting galvanic coatings was performed by using a contact classical profilometer Perthometer Concept Mahr with table Y-dnve PKT (Fig. 31).

Fig.31 *A pofile measurement gauge Perthometer Concept of the Mahr company [own investigations]*

The results will be presented in the form of a three-dimensional image - 3D was achieved using software PERTHOMETER CONCEPT v.6.50.

The results in the form of the three dimensional image - 3D and a curved share of the material in graphic form (Fig. 32, 33) was obtained using the software PERTHOMETER CONCEPT v.6.50.

Additionally to the quantitative description of surface roughness, chosen in accordance with PN-EN ISO 4287:1999 and PN-EN ISO 13565-2:1999 (defined parameters determined on the basis of the participation of material curve linearization), geometrical parameters: ***Ra*** - arithmetical mean deviation of the roughness profile , ***Mr1*** - material participation (in percent) determined by the intersection of the line separating the hills protruding from the roughness core profile and ***Mr2*** - material participation (in percentage) determined by the intersection of the line separating the deep recesses of the roughness core profile.

The core profile roughness means the roughness profile without distinctive hills and deep valleys.

AN ASSESSMENT OF THE SURFACE LAYER OF THE DISC GEOMETRY SAMPLES WITHOUT GALVANIC COATING

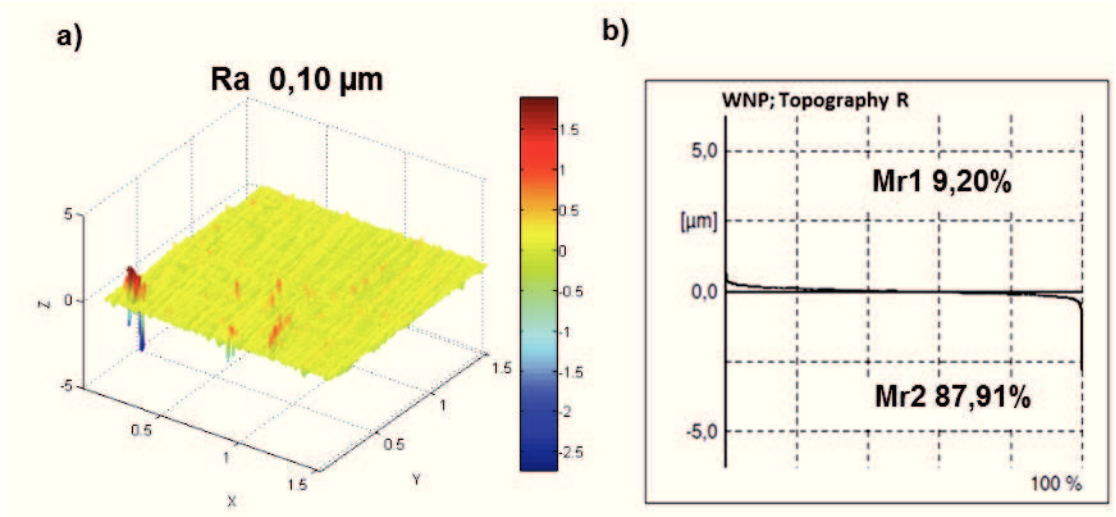

Fig.32 A profile of a sample of the disc geometry, a) the topography of the surface layer - 3D, b) curve share of the material of the sample geometry of the disc without the coating (after the process of grinding and polishing)

AN ASSESSMENT OF THE SURFACE LAYER OF THE PIPE GEOMETRY SAMPLES WITHOUT GALVANIC COATING

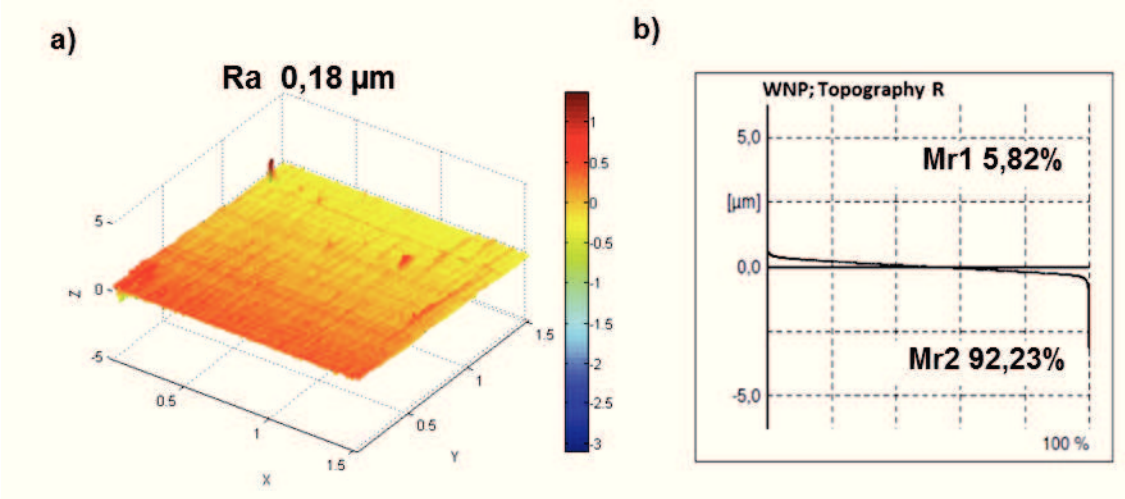

Fig.33 A profile of a sample of the pipe geometry, a) the surface layer topography - 3D, b) curve share sample material with a geometry pipe without coating (after grinding process)

8.6 Electrolytic metal coatings – Ni, Cr, Cu

An electrolytic coating was imposed according to the requirements of the standard PN-EN ISO 1456:2009 and PN-EN 1403: 2002 conventional galvanic baths as the corrosion protection of steel in the production of medical equipment.

Galvanic layers were applied to a steel substrate of the disc and a tube geometry (Fig.34) in the combinations shown in Table 9.

Table 9 Combinations of galvanic coatings for the disc and tube profile

Description of coatings	**Designation for disc**	**Designation for pipe**
	according to PN-EN ISO 1456:2009	
nickel-nickel-chromium	Fe//Ni20d/Cr	Fe//Ni20d/Cr
nickel-chromium	Fe//Ni10b/Crr	Fe//Ni10b/Crr
nickel-copper	Fe//Ni3s/Cub	Fe//Ni3s/Cub
copper	Fe//Cus	Fe//Cus

Where: **Fe –** mean substrate**, Ni -** nickel coating, **20 -** minimum thickness of nickel coating (20 μm)**, d –** nickel coating double layer called duplex, **b –** nickel coating single-layer with a minimum thickness 10 μm**, Crr –** standard chrome coating with a minimum thickness of 0,3 μm, **3 –** nickel coating thickness (3 μm), **s –** semi gloss nickel-layer coating**, Cub –** gloss copper, **Cus** – matte copper.

Plating a nickel-copper does not have its counterpart in the Polish standards.

Before the imposition multilayer coatings of metal samples were divided into 4 groups according to the determinations provided below:

- for samples with geometry of the disc:

0 - samples without coating

A - sample with coating nickel-nickel-chromium (Fe//Ni20d/Crr)

B - samples with coating nickel-chromium (Fe//Ni10b/Crr)

C - samples with coating nickel-copper (Fe//Ni3s/Cub)

D – samples with coating copper (Fe//Cus)

- for samples with pipe geometry:

R0 - samples without coating

I - sample with coating nickel-nickel-chromium (Fe//Ni20d/Crr)

II - samples with coating nickel-chromium (Fe//Ni10b/Crr)

III - a sample with coating nickel-copper (Fe//Ni3s/Cub)

IV - sample with coating copper (Fe//Cus)

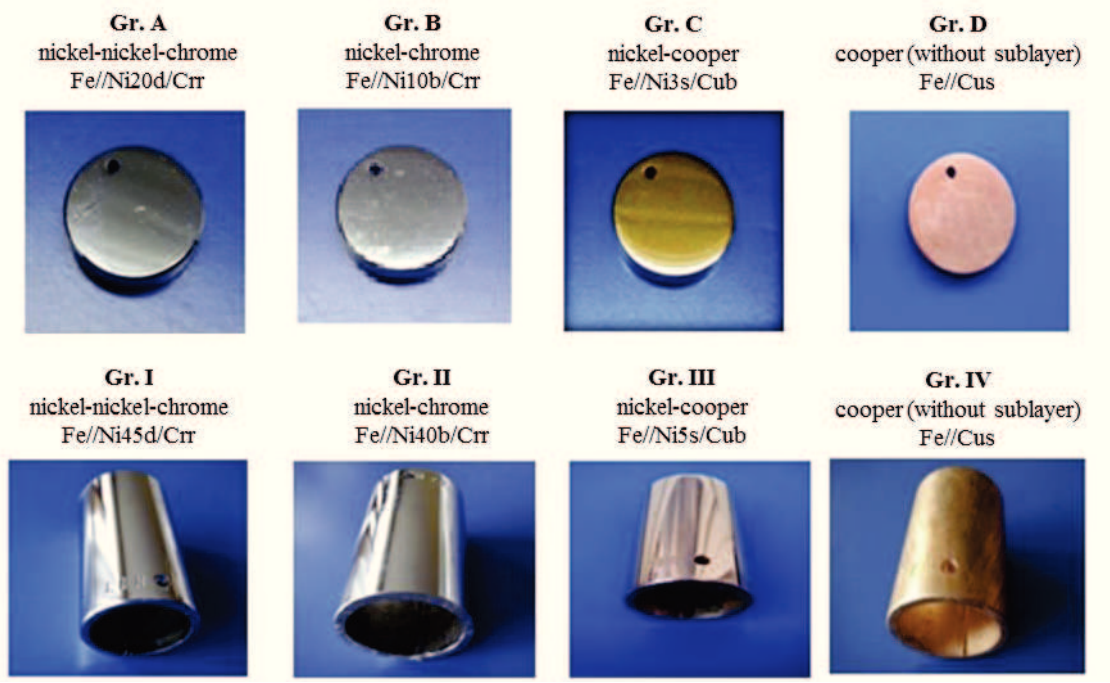

Fig.34 *The research material on disk geometry and pipes after the application of galvanic coatings divided into groups -a general view*

NICKEL COATING APPLICATION PROCESS

The imposition of electrolytic nickel coatings bath used Omega-Super (nickel semi-gloss) and SUPRAGAL 2000G (nickel gloss) developed by Dr.HESSE & CIE. The chemical composition shown in Table 10.

Table 10 The chemical composition of nickel bath semi-gloss Omega Super and gloss SUPRAGAL 2000G

Composition	The concentration range	The concentration during the process
Omega-Super		
nickel sulphate $NiSO_4$ x $6H_2O$	240÷300 g/dm^3	270 g/dm^3
nickel chloride $NiCl_2$ x $6H_2O$	40÷70 g/dm^3	60 g/dm^3
boric acid H_3BO_3	35÷50 g/dm^3	H_3BO_3 – 40 g/dm^3
potassium chloride KCl	0÷30 g/dm^3	20 g/dm^3
saccharin	0,2÷0,3 g/dm^3	0,3 g/dm^3
SUPRAGAL 2000G		
nickel sulphate $NiSO_4$ x $7H_2O$	240÷340 g/dm^3	280 g/dm^3
nickel chloride $NiCl_2$ x $6H_2O$	50÷80 g/dm^3	70 g/dm^3
boric acid H_3BO_3	35÷50 g/dm^3	40 g/dm^3
ions Cl	0÷30 g/dm^3	20 g/dm^3
ions Ni^{+2}	-	70 g/dm^3

The coatings applied to steel samples subjected to undergoing a prior treatment of mechanical and chemical preparation. Samples were suspended for technological hole copper wire Ø0,5 mm the copper hooks affixed to a copper cathode.

The coatings were applied in two combinations as triple - this applies to samples from group A and I and two-layer samples for group B and II (Fig.34).

Three-layer coating contains nickel semi-gloss (bath Omega-Super) glossy nickel (bath SUPRAGAL 2000G) and decorative chrome baths DC-700. The coating double layer consists of nickel glossy (bath SUPRAGAL 2000G) and decorative chromium (bath DC-700).

NICKEL PLATING IN OMEGA SUPER BATH

Degreased and pickled details (sample) were immersed in a bath of nickel Omega-Super and treated with electrolysis for 20 minutes according to the technology outlined in Table 11. By way of achieving a suitable thickness of the nickel layer. A manual controlled time may be modified depending on the thickness of the coating nickel pieces that took place in the case of the samples from the profile pipe in Group I and II. The nickel coating process for the samples of Group I and II of the pipe profile lasted for 40 minutes.

After applying the nickel layer semi-gloss, the samples were rinsed with demineralized water baths with a lower pH (pH 4,5). In order to impose a two-layer (group of samples B and II) or three-layer (group of samples A and I) samples were sent to the appropriate workstations. When applied the coatings gloss nickel so-called "duplex" details were placed in a bath SUPRAGAL 2000G. However, the sample group B and II were placed in a bath of chromium decorative DC-700.

Table 11 Technological parameters bath Omega-Super

Factor	**Range**	**The process of nickel plating of samples**
temperature	55 ÷ 60°C	58°C
pH	3,8÷4,4	4,5
current density	1÷8A/dm^2	4A/dm^2
voltage	3÷6 V	5V

NICKEL PLATING IN SUPRAGAL 2000G BATH

The process of nickel plating in a bath SUPRAGAL 2000G a glossy nickel was carried out as in a bath of Omega-Super. However, the nickel layer here is slimmer and, therefore, the process time was 10 minutes. Table 12 contains the baths parameters.

After imposition the nickel layer, the samples were rinsed in demineralized water with a lower pH (pH 4,5) and sent to the chroming bath.

Table 12 Technological parameters bath SUPRAGAL 2000G

Factor	**Range**	**The process of nickel plating of samples**
temperature	50 ÷ 60°C	55°C
pH	3,9÷4,8	4,4
current density	1÷8 A/dm^2	4 A/dm^2
voltage	3÷6 V	5 V

A DECORATIVE CHROME SAMPLE PROCESS OF STEEL GROUP A, B and I,II

A decorative chrome plating process was carried out in a chromic acid based bath, enriched with additives improving the ability of coverage and a speed of applying a coating. The bath composition chromium DC-700 company Atotech included in Table 13. The process of chrome plating was carried out directly after the nickel and rinsing. A bathtub with a capacity of 2,1 m^3 containing a chromium bath was made of sheet steel, chemical-resistant taped on the inside carpeted. The bath was equipped with a lead anode suspended on the copper rails, electric heaters and a temperature sensor. The bath temperature was measured continuously and automatically controlled by a thermostat.

The anodes are connected to the rectifier 3-phase, which is a source of direct current. Control of the parameters currents was manual. Current size of the galvanized samples were determined by the total area of the samples. For the samples tested it was 7 A/dm^2 (Table 14).

Following an application of the decorative chromium was performed in four stages chrome rinsing samples. The last stage was drying samples at 90° C for 3 minutes in an electric dryer controlled manually.

Table 13 The chemical composition of the chrome bath DC-700

Bath composition	**Concentration range**	**Concentration in the process**
chromic acid H_2CrO_4	160÷250 g/l	210 g/l
sulfuric acid H_2SO_4	0,8÷1,3 g/l	1,0 g/l
addition DC-1	30÷50 ml/l	40,0 ml/l
addition DC-2	25÷35 ml/l	30,0 ml/l

Table 14 Technological parameters of chrome plating steel samples from group A and I

bath temperature	31 ºC
current density	7 A/dm^2
process time	3 min

PROCESS COPPER PLATING

Copper plating was carried out in two groups of samples C, D, and group III and IV. Group C and III were treated by applying a coating of copper plating with a high gloss (shiny) on the sub-layer of nickel. For sample D, and IV the group also applied by electrolysis method copper coating matte directly to the substrate, using alkaline solutions based on cyanides.

COATING - COPPER HIGH GLOSS

The imposition of high gloss copper was used in the RUBIN WK bath, whereas the bath for the nickel plating semi-gloss (nickel base) is a PRE-SIRIUS. Both baths are made with Metallchemie Chemische Fabrik. The chemical composition and process parameters are shown in Table 15 and 16**.**

The samples after the mechanical preparation before the coating application process were suspended with a copper wire Ø0,5 mm for the hole technology for copper hooks affixed to a copper cathode. Below shows a description of the process of applying a coating of copper with a sub-layer of nickel:

- chemical degreasing process (time 1 minute, temp.42 °C)
- degreasing electrochemical (cathodic degreasing time 5 s, anodic time 10 s, temp. 60 °C),
- rinsing first (running water) time 5s, temp. 20 °C
- second rinsing (running water) time 5s, temp. 20 °C
- pickling in HCl 7 % , time 5min, temp. 20 °C
- rinsing first (running water) time 5 s, temp. 20 °C
- second rinsing (running water) time 5 s, temp. 20 °C
- activation of the surface of the salt activation (chemical composition is secret manufacturer), time 5 min, temp. 20 °C
- rinsing in demineralized water, time 5 s temp. 20 °C
- electroplating nickel plating (nickel base), time 7 min, temp. 50 °C, the direct current density 3,5 A/dm^2 - rinsing in demineralized water, , time 2 s, temp. 20 °C
- electroplating copper plating, time 40 min to the assumption that the coating will be about 10 μm, temp. 25 °C
- first rinsing in demineralized water, 3 s, temp. 20 °C
- second rinsing in demineralized water, 3 s, temp. 20 °C
- drying process (final stage), time 10 min, temp. 80 °C

Table 15 The chemical composition of the bath PRE-SIRIUS to the semi-gloss nickel plating (nickel base) and copper RUBIN WK

Composition	Concentration range	Concentration in the process
Both PRE-SIRIUS		
Nickel (Ni^{+2})	60÷90 g/dm^3	80 g/dm^3
Chloride (Cl^-)	15÷25 g/dm^3	20 g/dm^3
boric acid (H_3BO_3)	40÷55 g/dm^3	50 g/dm^3
Both RUBIN WK		
copper (Cu)	50÷60 g/dm^3	55 g/dm^3
sulfuric acid (H_2SO_4)	50÷60 g/dm^3	55 g/dm^3
Chloride (Cl^-)	30÷150 mg/dm^3	80 mg/dm^3

Table 16 The technological parameters of the semi-gloss nickel plating and copper plating steel samples of group C and III

Nickel plating on semi-gloss	
bath temperature	50 °C
cathodic current density	3,5 A/dm^2
process time	7 min
pH	4,1
Copper plating	
bath temperature	25 °C
cathodic current density	4,0 A/dm^2
process time	40 min

COPPER COATING - MATT

The process of copper plating in an alkaline cyanide bath of steel samples of group D and IV was made by electrolysis. The chemical composition and process parameters are included in Table 17 and 18.

The technological process included the following:

- mechanical surface preparation
- electrolytic degreasing in an alkaline bath at the temperature of about 70 °C
- rinsing in hot temperature of 50-60 °C
- pickling in hydrochloric acid solution at ambient temperature
- rinsing at ambient temperature
- copper plating in a cyanide bath
-multi-stage rinsing in water.

Table 17 The chemical composition of cyanide bath

Composition	**Concentration range**	**Concentration in the process**
Copper cyanide (I) CuCN	14÷30 g/dm^3	25 g/dm^3
Sodium cyanide NaCN	25÷52 g/dm^3	45 g/dm^3
Sodium carbonate Na_2CO_3	15÷70 g/dm^3	15 g/dm^3
Sodium hydroxide NaOH	to pH 12	pH 12

Table 18 The copper plating process parameters without a sub-layer for steel samples from Group D and IV

bath temperature	ambient temperature
cathodic current density	0,7 A/dm^2
process time	35min

8.7 Evaluation of the surface layer of metallic coatings imposed

The study of the geometrical structure of the surface layer of the electroplated coatings imposed on the sample profile of the disc (Ø14,6 mm) and the pipe (Ø28x2, 5x50 mm), was performed by using a contact profilometer Perthometer Concept Mahr with table Y-dnve PKT.

The results of measurements in 3D and curves in participation of material in graphic form (Figure 34-41) was determined using the software Perthometer CONCEPT v.6.50, as mentioned earlier on page 61.

AN EVALUATION OF THE SURFACE LAYER NICKEL-NICKEL-CHROME COATING ON A SAMPLE OF A GEOMETRY DISC

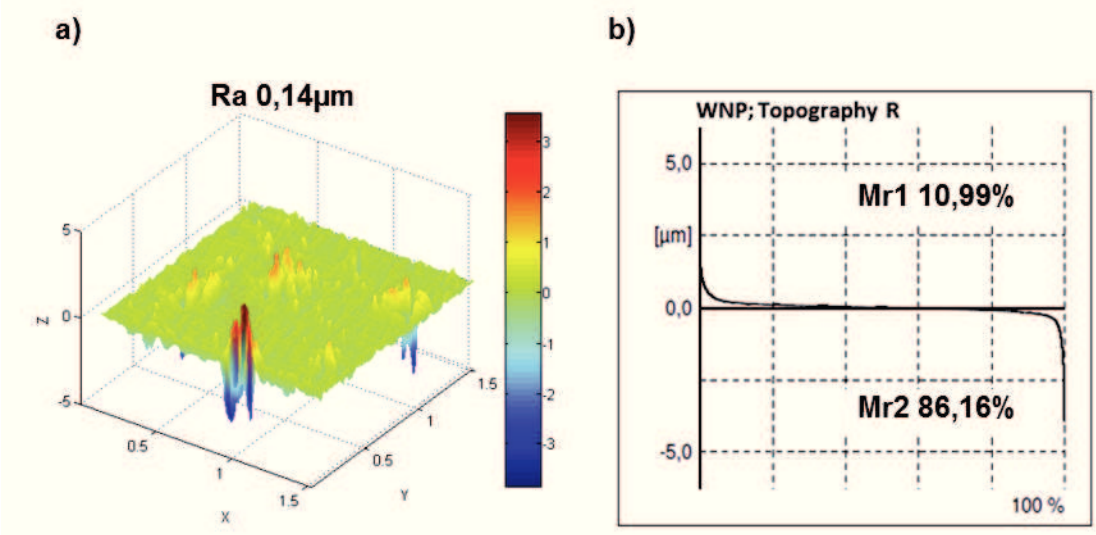

Fig.35 A sample the geometry of the disc with nickel -nickel-chromium coating, a) topography of the surface layer in terms of 3D, b) the curve participation of material

AN EVALUATION OF THE SURFACE LAYER NICKEL-CHROME COATING ON A SAMPLE OF GEOMETRY DISC

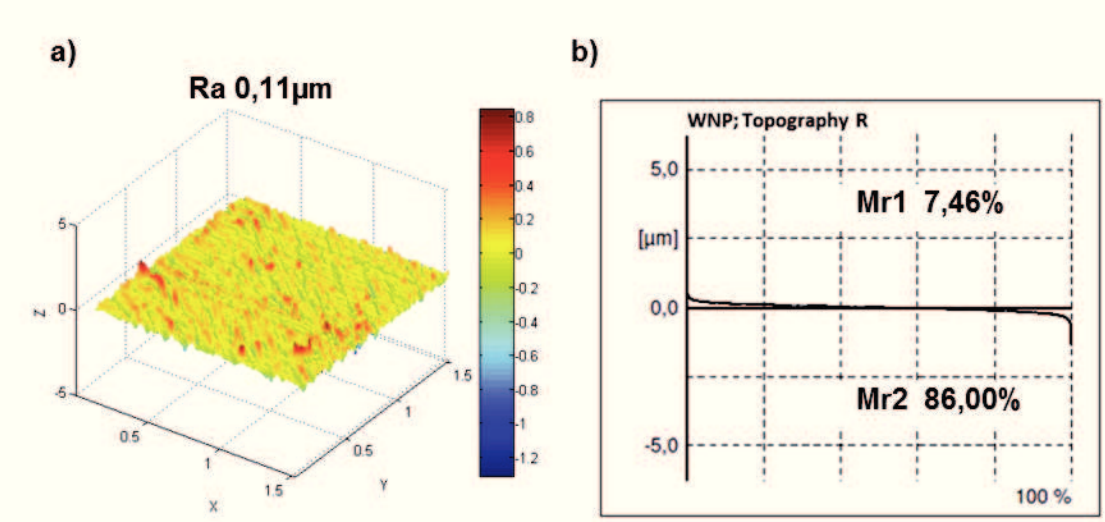

Fig.36 A sample of a geometry disk with a nickel-chrome coating, a) topography of the surface layer in terms of 3D, b) the curve participation of material

AN EVALUATION OF THE SURFACE LAYER NICKEL-COPPER COATING ON A SAMPLE OF A GEOMETRY DISC

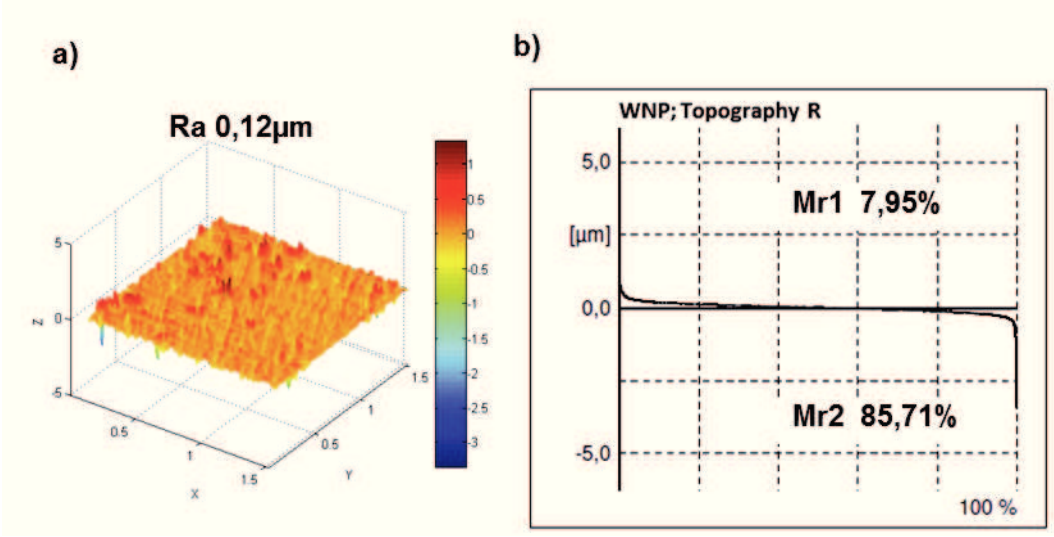

Fig.37 A sample of a geometry disk with a nickel-copper coating, a) topography of the surface layer in terms of 3D, b) the curve of participation of the material

AN EVALUATION OF THE SURFACE LAYER OF COPPER COATING ON A SAMPLE OF A GEOMETRY DISC

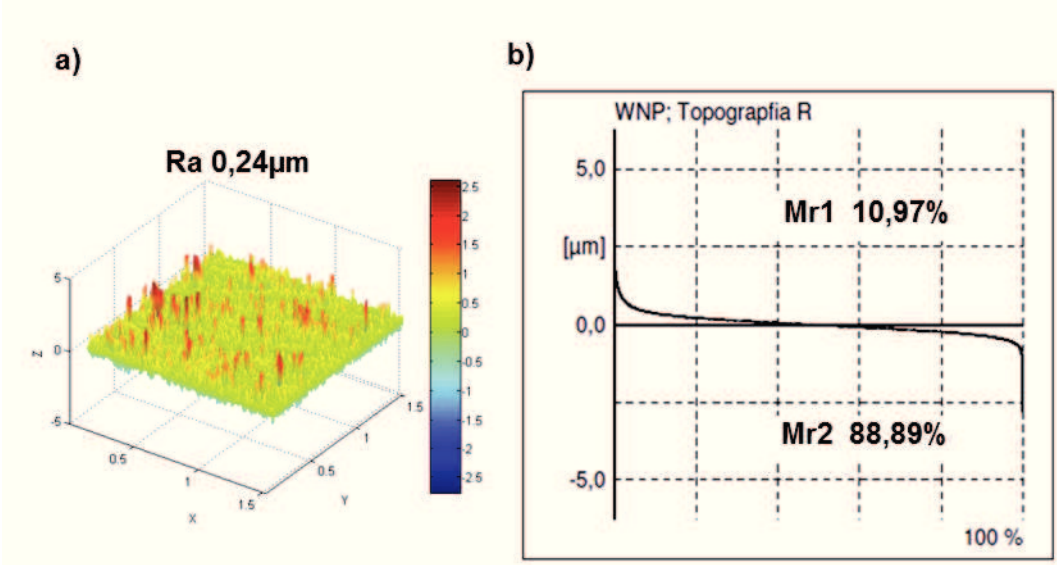

Fig.38 A sample of a geometry disk with a copper coating, a) topography of the surface layer in terms of 3D, b) the curve of participation of the material

AN EVALUATION OF THE SURFACE LAYER NICKEL-NICKEL-CHROME COATING ON A SAMPLE OF THE GEOMETRY PIPE

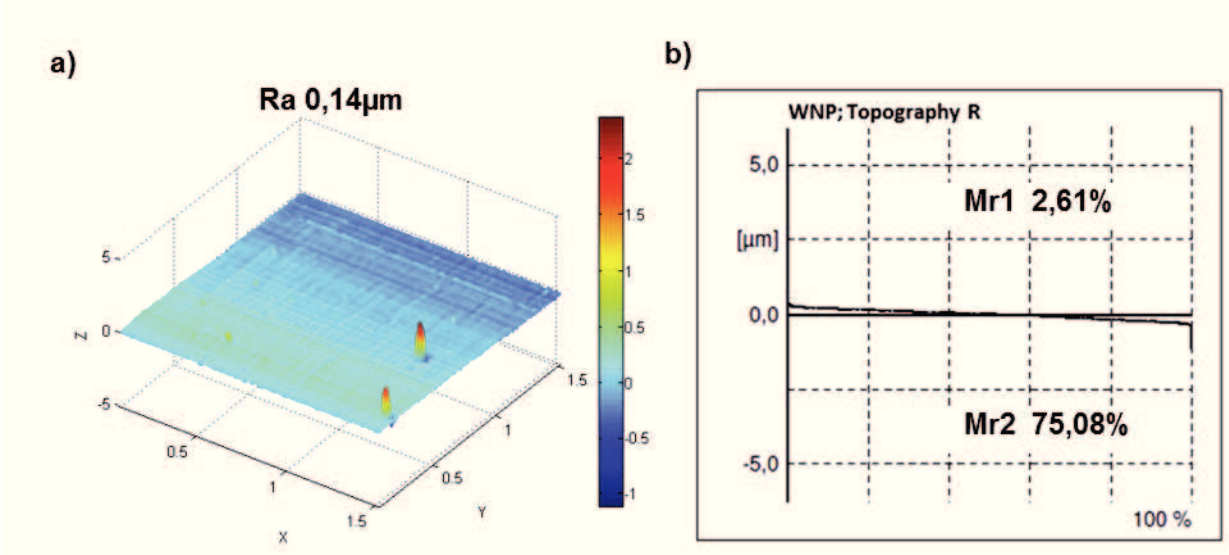

Fig.39 A sample of a geometry pipe with a nickel-nickel-chrome coating, a) topography of the surface layer in terms of 3D, b) the curve of participation of the material

AN EVALUATION OF THE SURFACE LAYER NICKEL-CHROME COATING ON A SAMPLE OF GEOMETRY PIPE

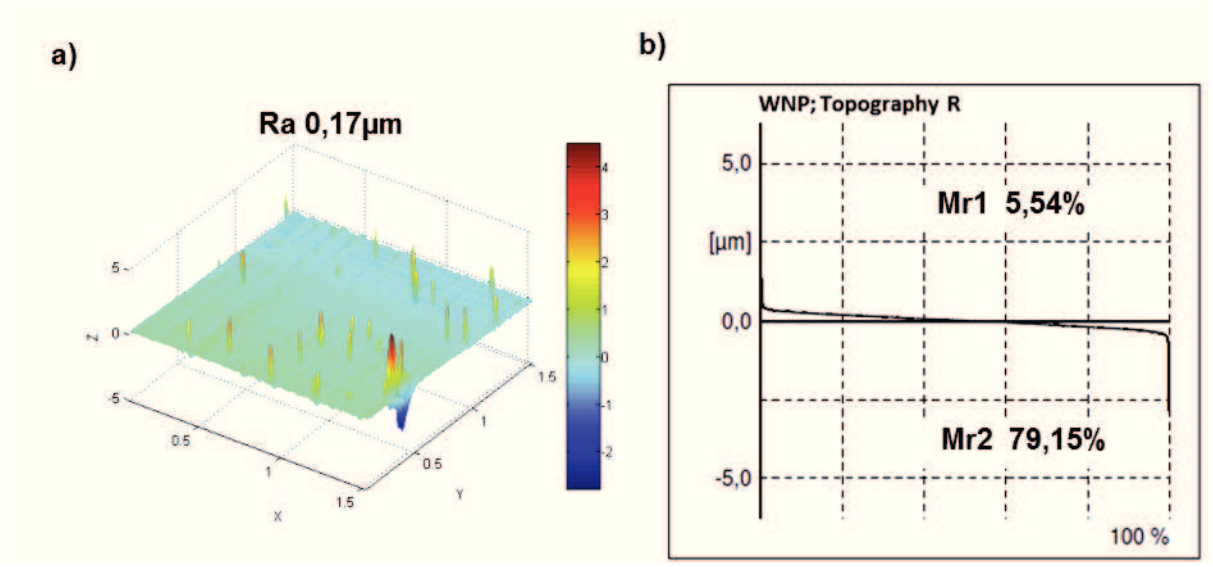

Fig.40 A sample geometry pipe with a nickel-chrome coating, a) topography of the surface layer in terms of 3D, b) the curve of participation of the material

AN EVALUATION OF THE SURFACE LAYER NICKEL-COPPER COATING ON A SAMPLE OF GEOMETRY PIPE

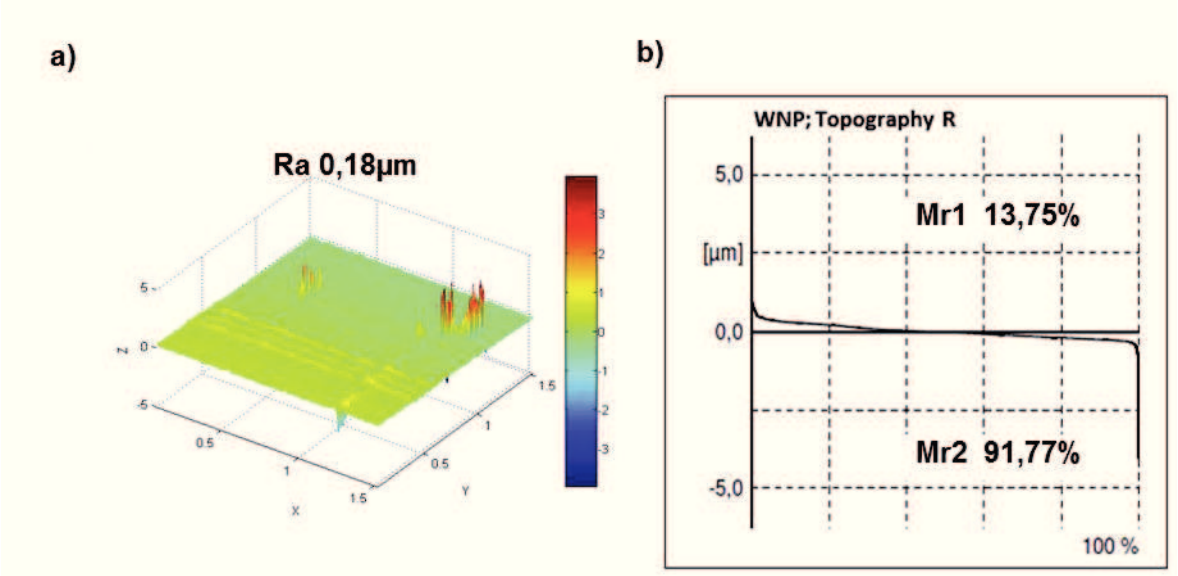

Fig.41 A sample of the geometry pipe with a nickel-copper coating, a) topography of the surface layer in terms of 3D, b) the curve of participation of the material

AN EVALUATION OF THE SURFACE LAYER OF THE COPPER COATING ON A SAMPLE OF GEOMETRY PIPE

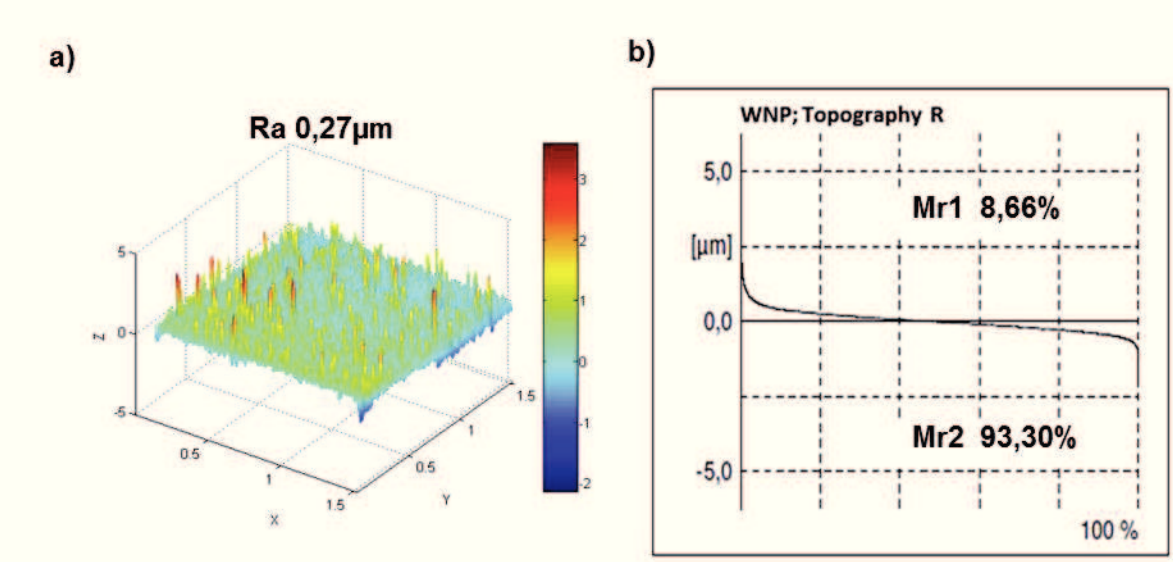

Fig.42 A sample of the geometry pipe a with copper coating, a) topography of the surface layer in terms of 3D, b) the curve of participation of the material

8.8 Metallographic tests

Metallographic tests will be performed on samples of steel in the form of discs of Ø14,6 mm (Fig. 26, page 56) - DC01 steel and tube samples Ø28x2,5x50 mm - stainless RSt37 NBK-2 (Fig. 43), with superimposed metallic coatings.

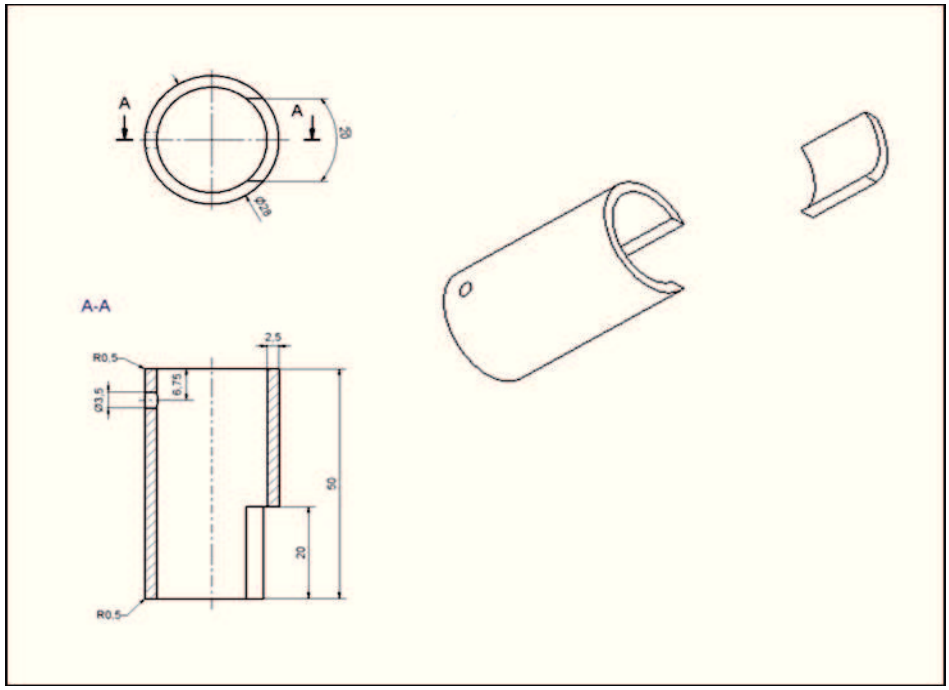

Fig.43 Place cut-out section with pipe Ø28x2, 5x50mm - steel RSt37-2 NBK intended for metallographic tests

Prepared metallographic specimen (Fig. 44) was to observation the macro, microscopic and X-ray microanalysis. Directly before the metallographic testing surface layer were etch nital (3% solution of nitric acid in ethanol).

Microscopic analyses of the steel structure for samples of the disc and pipes profile were made according to standard PN-EN ISO 643:2005 on metallographic microscope Carl Zeiss AxioImager. M1m at a magnification of 100, 500 and 1000x.

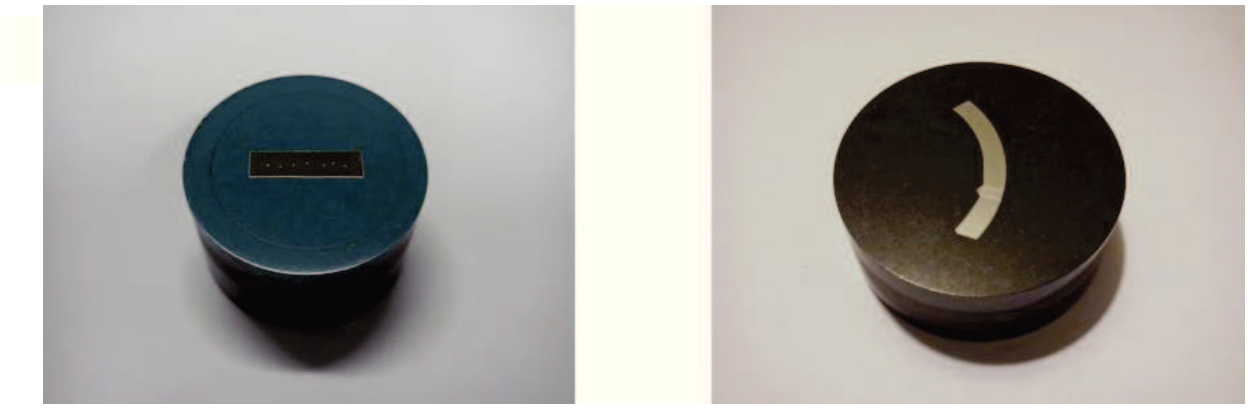

Fig.44 Made metallographic specimen, a) disc Ø14,6 mm, b) fragment from the pipe 20x20 mm [own investigations]

MICROSCOPIC METALLOGRAPHY SAMPLES OF GEOMETRY DISC

Microscopic analysis of steel at a magnification of 100, 500 and 1000x for samples of the geometry disk shows the structure of ferrite grain fine and evenly distributed. Cementite spherical separation was also observed uniformly distributed inside the grains and insignificant quantities plate cementite at the grain boundary (Fig. 45).

The structure of a typical cold-rolled low-carbon steel, alloy steels for cold forming (e.g., bending, stamping).

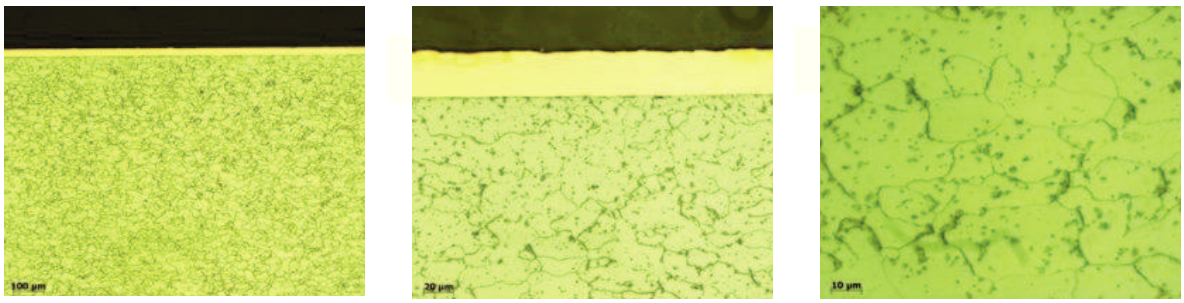

Fig.45 A microstructure of DC01 steel – a disk profile was digested nital a) 100x magnification, b) 500x magnification, c) 1000x magnification [own investigations]

MICROSCOPIC METALLOGRAPHY SAMPLE OF THE PIPE GEOMETRY

A microscopic analysis of steel at a magnification of 100x, 500x and 1000x for the sample pipe geometry shows the structure of ferrite grain fine evenly distributed. The spin cementite ball evenly distributed the grains inside and insignificant quantities cementite plate at the grain boundary (Fig. 46).

The structure is similar to flat samples.

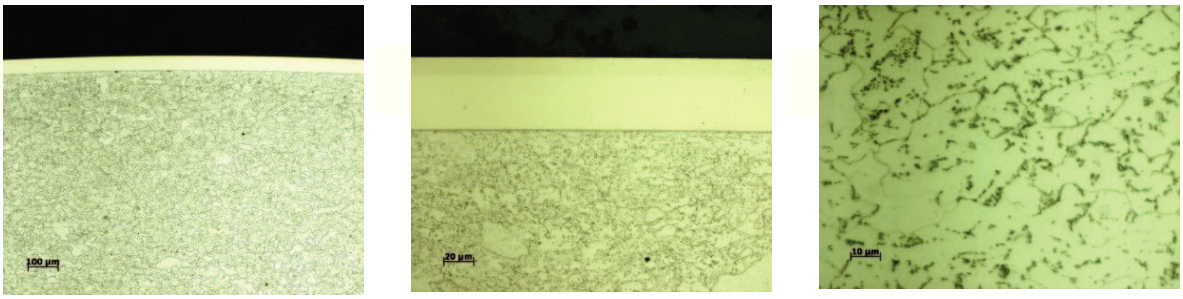

Fig.46 A microstructure of steel RSt37-2 NBK – a profile pipe was digested nital, a) 100x magnification, b) 500x magnification, c) 1000x magnification [own investigations]

AN EVALUATION OF THE QUALITY SIZE OF THE GRAIN PRESENT IN THE MATERIAL RESEARCHED

The micrographic designation of grain size for the DC01 and RSt37-2 NBK was performed on metallurgical microscope Carl Zeiss AxioImager.M1m according to PN-EN ISO 643:2005-table 19.

Table 19 Grain size according to EN ISO 643:2005 for DC01steel and RSt37-2 NBK steel

Steel DC01 - No sample	**No pattern according to PN-EN ISO 643:2005**
11	7,5
21	7,5
31	7,5
71	7,5
Steel RSt37-2 NBK – No sample	**No pattern according to PN-EN ISO 643:2005**
R15	7,5
R25	7,5
R35	7,5
R75	7,5

METALLIC COATING MEASUREMENT THICKNESS

Measuring the thickness of galvanic coatings produced (Table 20 and 21), and their adhesion to the metal substrate for the profile disk and pipe was analyzed using metallographic microscope Carl Zeiss AxioImager.M1m at a magnification of 500 and 1000X (Fig. 46, 47, 48, 49).

A MEASUREMENT THICKNESS COATINGS AND ADHESION TO THE METALLIC SUBSTRATE FOR THE PROFILE DISCK

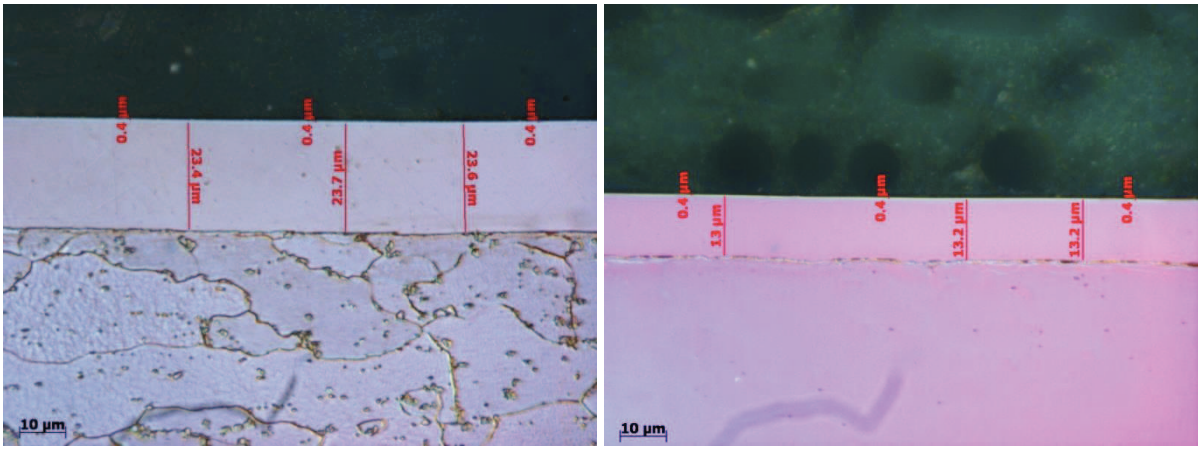

Fig.47 A microscopic measurement thickness coatings and adhesion to the metallic substrate, a) nickel-nickel-chrome (Fe//Ni20dCrr), b) nickel-chrome (Fe//Ni10bCrr) – profile disc

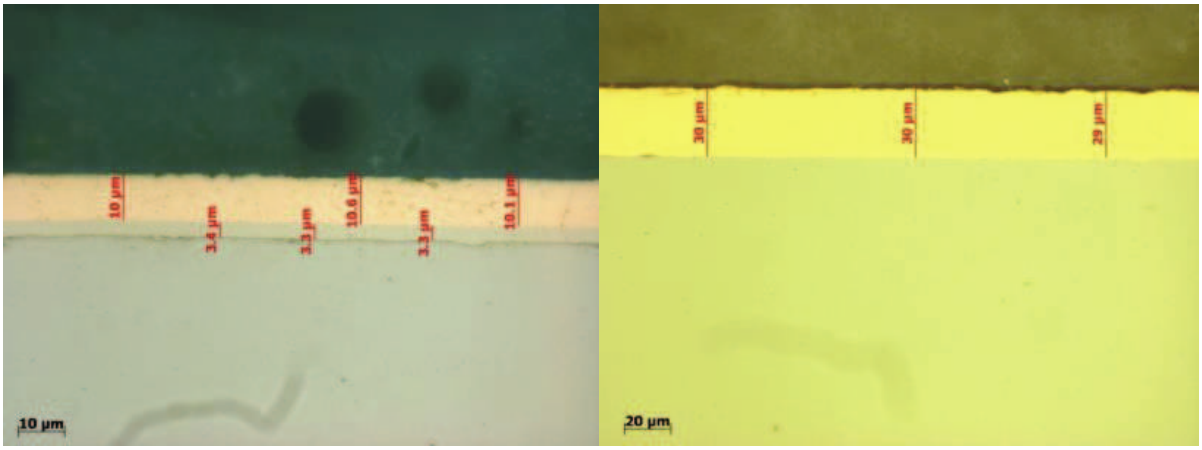

Fig.48 A microscopic measurement thickness coatings and adhesion to the metallic substrate, a) nickel-copper (Fe//Ni3sCu), b) copper Fe//Cup) – profile disc

A MEASUREMENT OF THE THICKNESS OF THE COATINGS AND THE ADHESION TO THE METALLIC SUBSTRATE FOR THE PROFILE PIPE

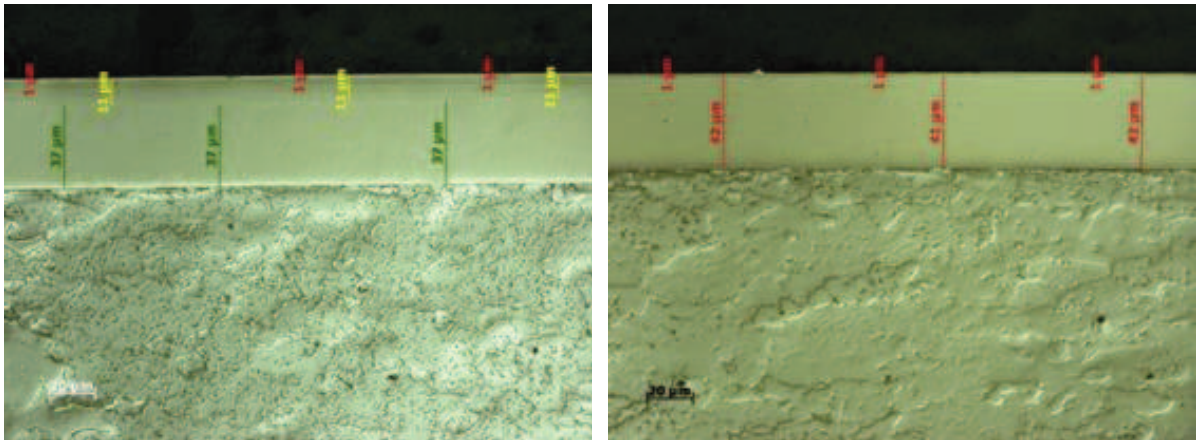

Fig.49 A microscopic measurement thickness coatings and adhesion to the metallic substrate, a) nickel-nickel-chrome (Fe//Ni48dCrr), b) nickel-chrome (Fe//Ni40bCrr) – profile pipe

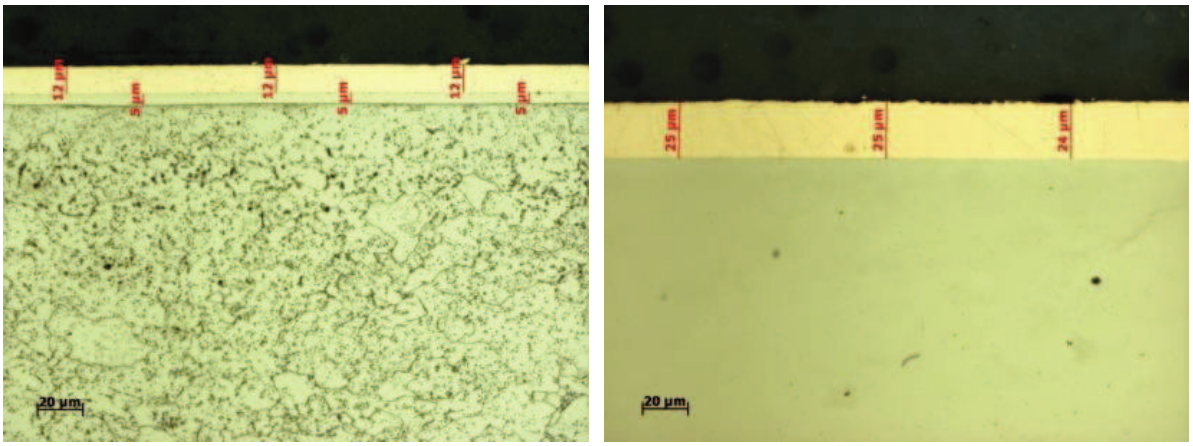

Fig.50 A microscopic measurement thickness coatings and adhesion to the metallic substrate, a) nickel-copper (Fe//Ni5sCub), b) copper (Fe//Cup) – and profile pipe

Table 20 The results of the measurement thickness galvanic layer for samples profile disk and pipe

Sample number	Layer	Layer thickness [µm]			Maximum thickness [µm]	Minimum thickness [µm]	Average value [µm]	Standard deviation
Profile disc								
11	**nickel-nickel**	23,4	23,7	23,6	23,7	23,4	23,6	0
	chrome	0,4	0,4	0,4	0,4	0,4	0,4	0
21	**nickel**	13,0	13,2	13,2	13,2	13,0	13,1	0
	chrome	0,4	0,4	0,4	0,4	0,4	0,4	0
31	**nickel**	3,4	3,3	3,3	3,4	3,3	3,3	0
	copper	10,0	10,6	10,1	10,6	10,0	10,2	0
710	**copper**	30,0	30,0	29,0	30,0	29,0	29,7	1
Profile pipe								
R12	**nickel**	37,0	37,0	37,0	37,0	37,0	37,0	0
	nickel	11,0	11,0	11,0	11,0	11,0	11,0	0
	chrome	1,0	1,0	1,0	1,0	1,0	1,0	0
R21	**nickel**	42,0	41,1	42,0	42,0	41,0	41,7	0
	chrome	1,0	1,0	1,0	1,0	1,0	1,0	0
R32	**nickel**	5,0	5,0	5,0	5,0	5,0	5,0	0
	copper	12,0	12,0	12,0	12,0	12,0	12,0	0
R74	**copper**	25,0	25,0	24,0	25,0	24,0	24,7	1

Table 21 Average values of coating thickness for different combinations

Combination of coatings	Average thickness of the coatings -profile disc [µm]	Average thickness of the coatings - profile pipe [µm]
nickel-nickel-chrome	24,0	49,0
nickel-chrome	13,5	42,7
nickel-copper	13,5	17,0
copper	29,7	24,7

A SUBSTRATE HARDNESS MEASUREMENT

A hardness of the steel substrate samples of the disc and tube geometry was performed by classical on a universal hardness tester Zwick / Roell ZHU-250, PN-EN ISO 6507-1:2007 (Fig. 51). Was used with a load equal to HV 1. HV 1 means that the test was conducted at a load of 1 kgf, (1kgf - one kilogram-force, 1kgf = 9,80665 N).

The results of the hardness measurement are shown in Table 22 and Figure 52.

Fig.51 A universal hardness tester Zwick / Roell ZHU250 [own investigations]

Table 22 Results of the hardness measurement of the substrate samples geometry of the disc and pipe

Sample number	Hardness [HV1]					Max. [HV1]	Min. [HV1]	The average hardness [HV1]	Standard Deviation
Steel DC01 (disk geometry)									
11	109	111	106	113	111	113	106	110	3
12	103	107	105	103	105	107	103	105	2
21	104	102	107	102	102	107	102	103	2
22	103	105	107	110	114	114	103	108	4
31	105	101	101	102	104	105	101	103	2
32	106	106	102	103	107	107	102	105	2
Steel RSt37-2 NBK (pipe geometry)									
R01	137	137	143	145	141	145	137	141	4
R12	139	139	140	139	141	141	139	140	1
R21	138	139	143	145	142	143	138	141	3
R32	137	142	141	141	144	144	137	141	3
R74	141	137	138	139	141	141	137	139	2
R75	141	144	140	138	138	144	138	140	2

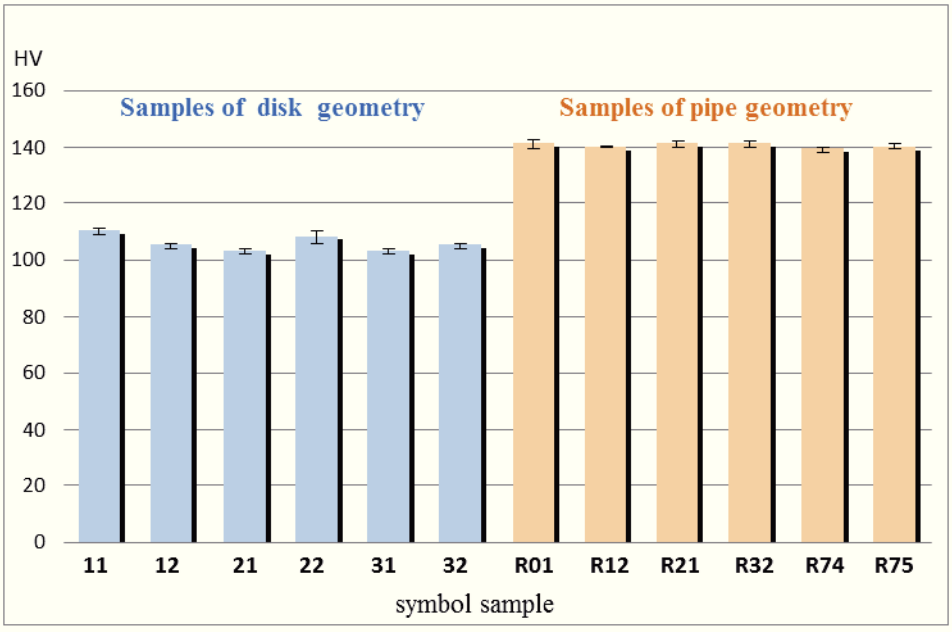

Fig.52 Hardness measurements taking into account the standard deviation

8.9 X-ray microanalysis

An x-ray microanalysis point of the chemical composition of the substrate and coating was made by an electron microprobe JEOL model JXA-733 (Fig. 53).

Metallographic specimen were subjected to analysis cross the sections of the geometry of the disc - DC01 steel, with multi-layered metallic coatings.

The analysis was conducted at an 15 kV accelerating voltage. The results are presented graphically in the form of graphs, X-ray energy spectrum - EDS (Energy dispersive spectroscopy.

The results of the observation and analysis of the test micro-areas of the selected samples in the drawings from 54 to 77 and tables 23 to 26.

Fig.53 Electron microprobe JEOL JXA-733 model [own investigations]

AN X-RAY MICROANALYSIS SAMPLE WITH NICKEL- NICKEL-CHROME COATING (Fe//Ni20dCr)

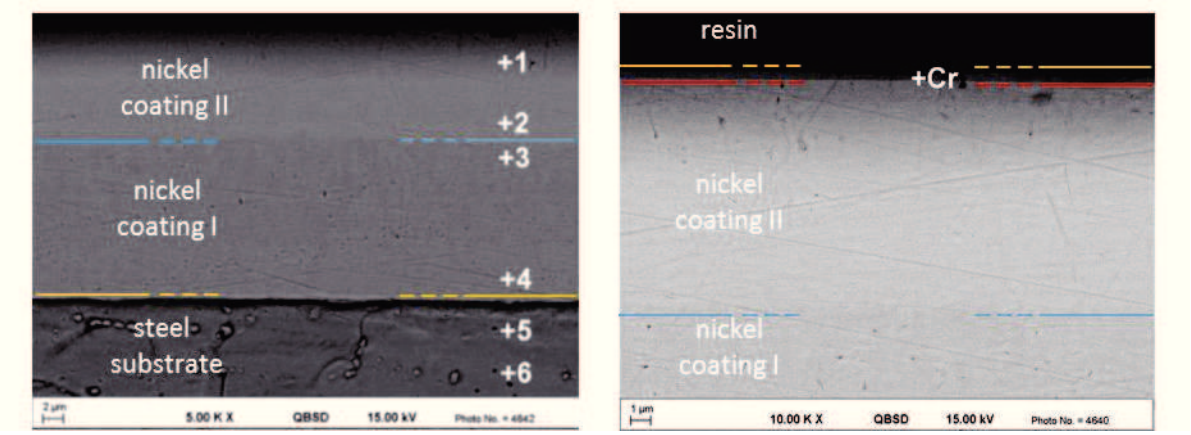

Fig.54 X-ray microanalysis steel points - point 5,6 and nickel coating I - point 3,4 and nickel II - point 1,2 - 5000x magnification and point + Cr. 10000x magnification

Table 23 Chemical microanalysis results for a cross section on the border layers of nickel-nickel-chrome (Fe//Ni20dCr)

Analyzed element	**Place of analysis**						
	1	2	3	4	5	6	+Cr
	Content in [%] by weight.						
Fe	0,00	0,00	0,00	1,91	100,00	100,00	0,00
Ni	100,00	100,00	100,00	98,09	0,00	0,00	9,83
Cr	0,00	0,00	0,00	0,00	0,00	0,00	90,17

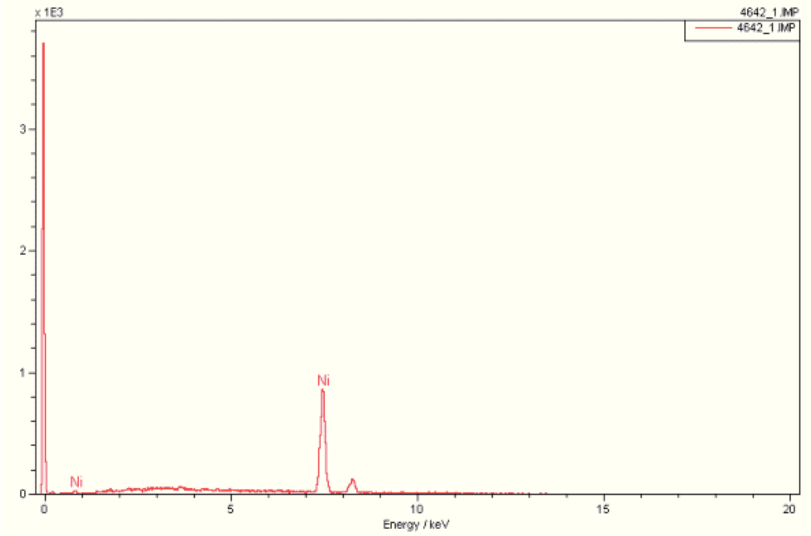

Fig.55 An x-ray energy spectrum obtained from the layer of nickel II - point 1

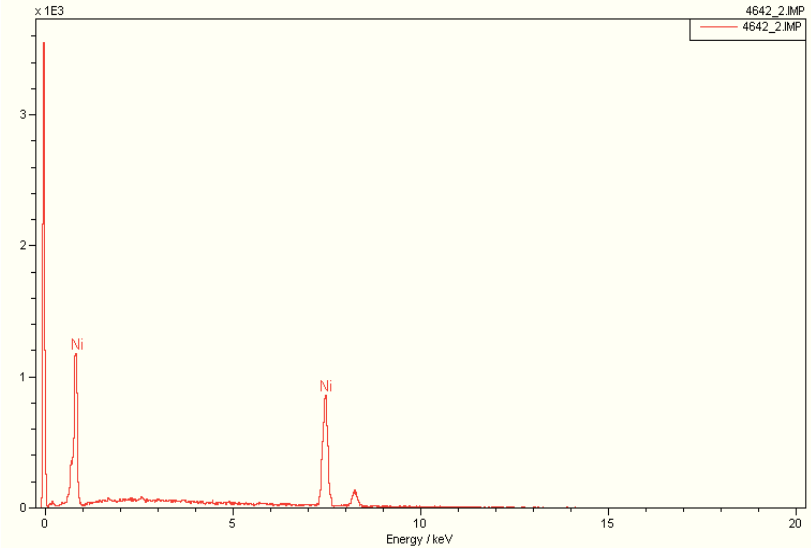

Fig.56 An x-ray energy spectrum obtained from the layer of nickel II - point 2

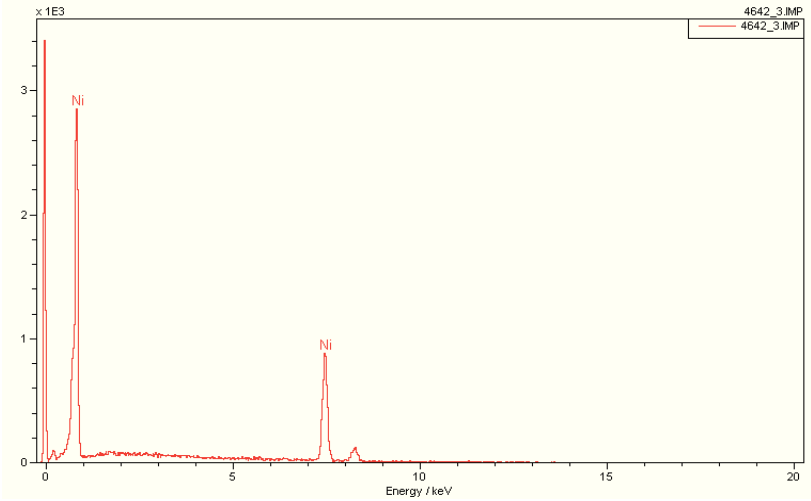

Fig.57 An x-ray energy spectrum obtained from the layer of nickel I - point 3

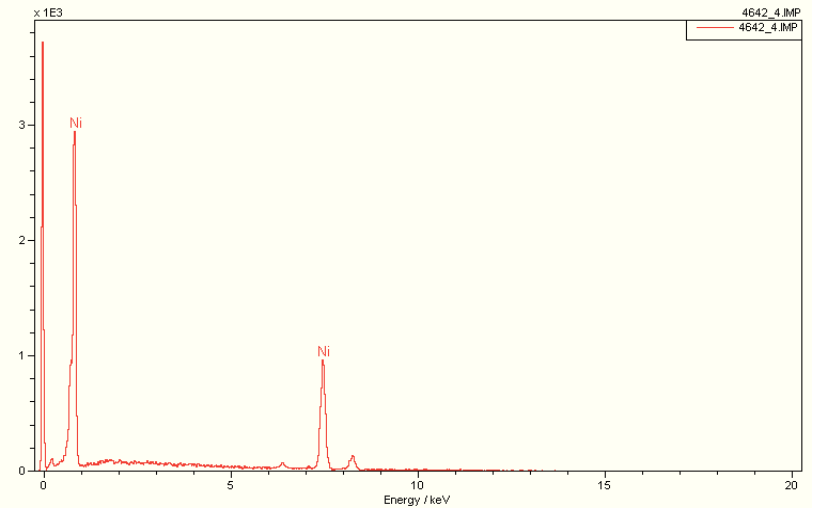

Fig.58 *An x-ray energy spectrum obtained from the layer of nickel I - point 4*

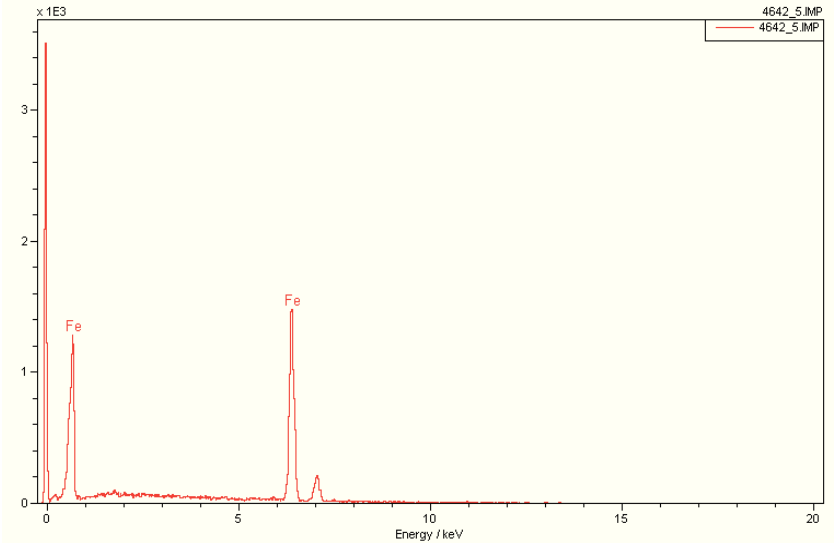

Fig.59 An x-ray energy spectrum obtained from the steel substrate - point 5

AN X-RAY MICROANALYSIS SAMPLE WITH NICKEL-CHROME COATING (Fe//Ni10bCrr)

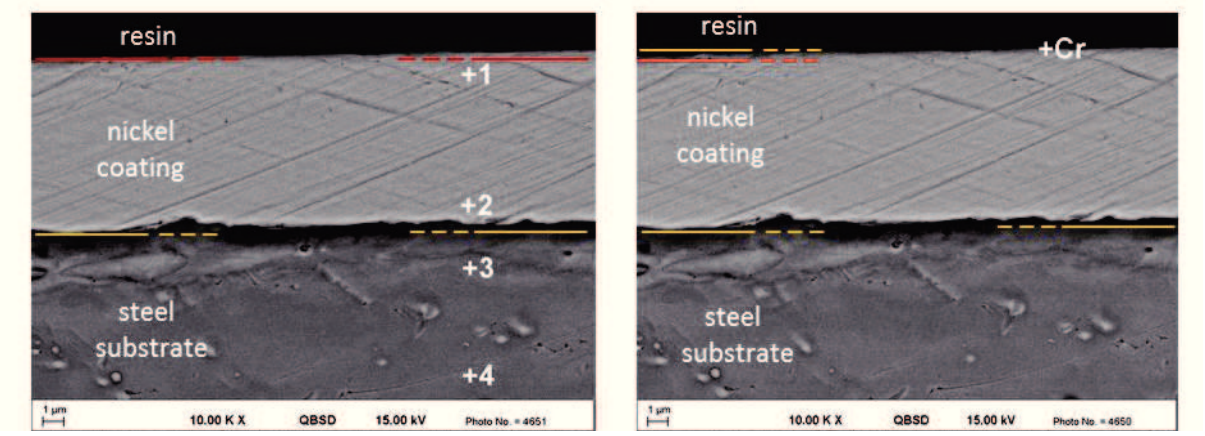

Fig.60 X-ray microanalysis steel points - point 3,4 and nickel coating - point 1,2 and point + Cr. 10000x magnification

Table 24 Chemical microanalysis results for a cross section on the border layers of nickel-chrome (Fe//Ni10bCrr)

Analyzed element	**Place of analysis**				
	1	2	3	4	+Cr
	Content in [%] by weight.				
Fe	1,25	2,37	97,31	100,00	0,00
Ni	98,75	97,63	2,69	0,00	81,86
Cr	0,00	0,00	0,00	0,00	5,92
Ca	0,00	0,00	0,00	0,00	3,18
Al	0,00	0,00	0,00	0,00	4,30
Si	0,00	0,00	0,00	0,00	4,74

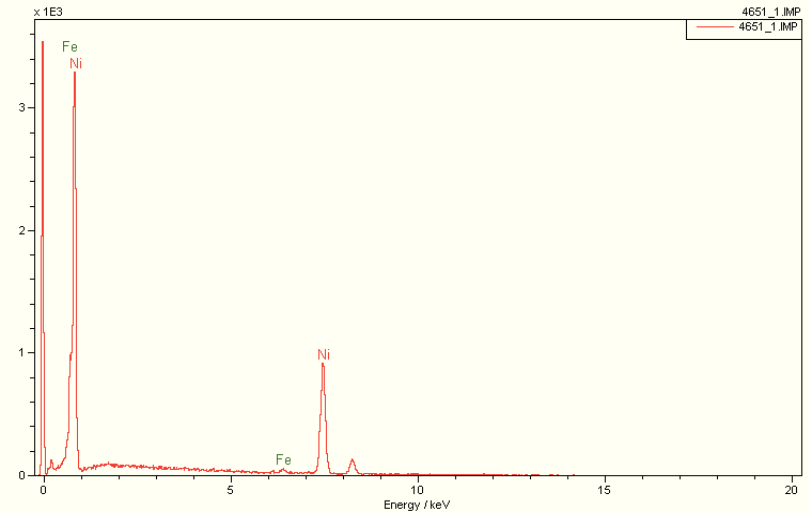

Fig.61 *An x-ray energy spectrum obtained from the nickel layer - point 1*

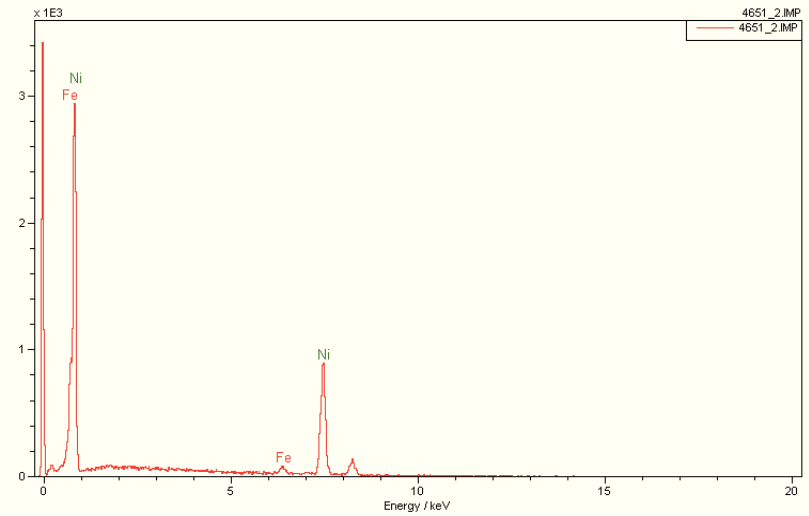

Fig.62 *An x-ray energy spectrum obtained from the nickel layer - point 2*

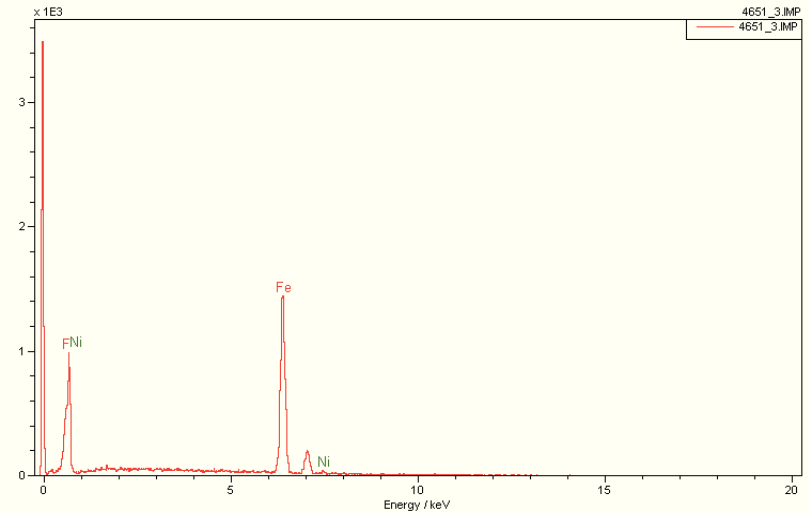

Fig.63 *An x-ray energy spectrum obtained from the steel substrate - point 3*

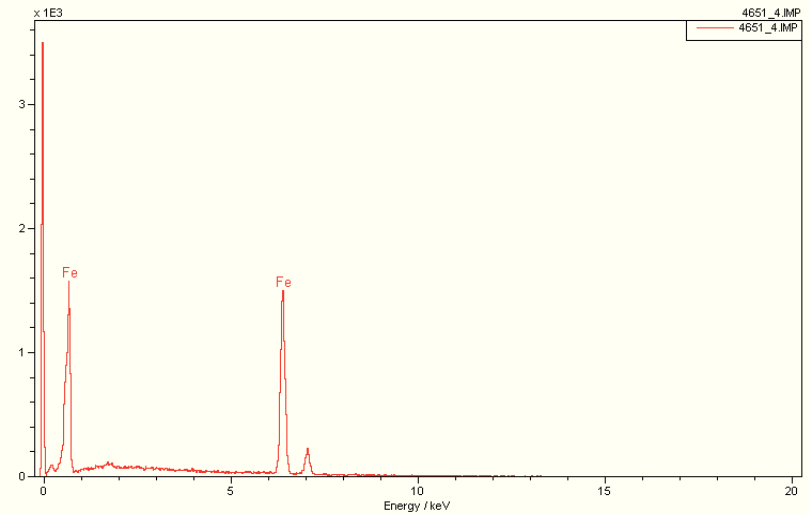

Fig.64 An x-ray energy spectrum obtained from the steel substrate - point 4

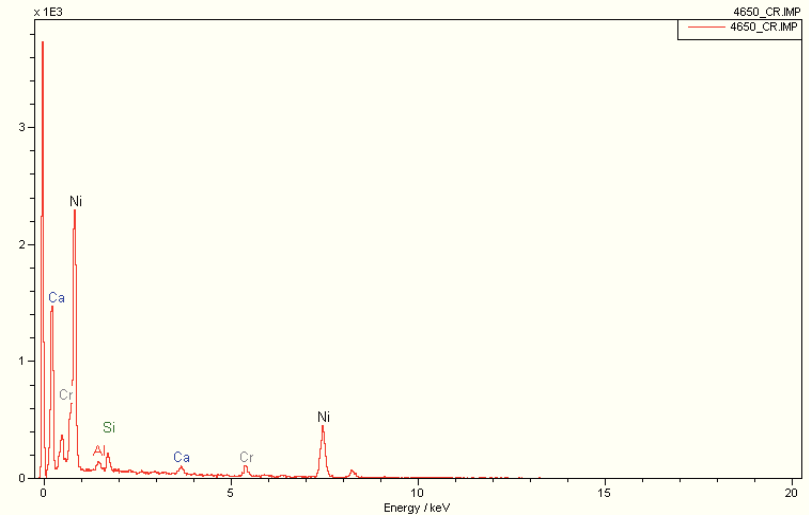

Fig.65 An x-ray energy spectrum obtained from the chromium layer - point +Cr

AN X-RAY MICROANALYSIS SAMPLE WITH NICKEL-COPPER COATING (Fe//Ni5sCub)

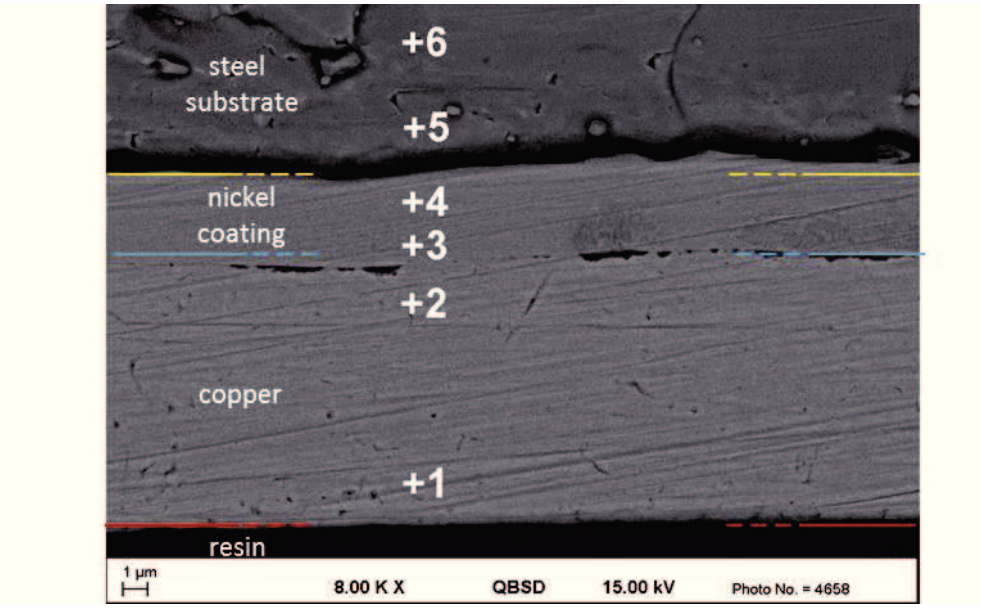

Fig.66 X-ray microanalysis steel points - point 5,6 and nickel coating - point 3,4 and copper coating - point 1,2. 8000x magnification

Table 25 Chemical microanalysis results for a cross section on the border layers of nickel-copper (Fe//Ni5sCub)

Analyzed element	**Place of analysis**						
	1	2	3	4	5	6	7
	Content in [%] by weight.						
Fe	0,00	0,00	2,41	3,01	98,77	100,00	-
Ni	0,00	0,00	90,27	96,99	1,23	0,00	-
Cu	100,00	100,00	6,48	0,00	0,00	0,00	-
Mo	0,00	0,00	0,97	0,00	0,00	0,00	-

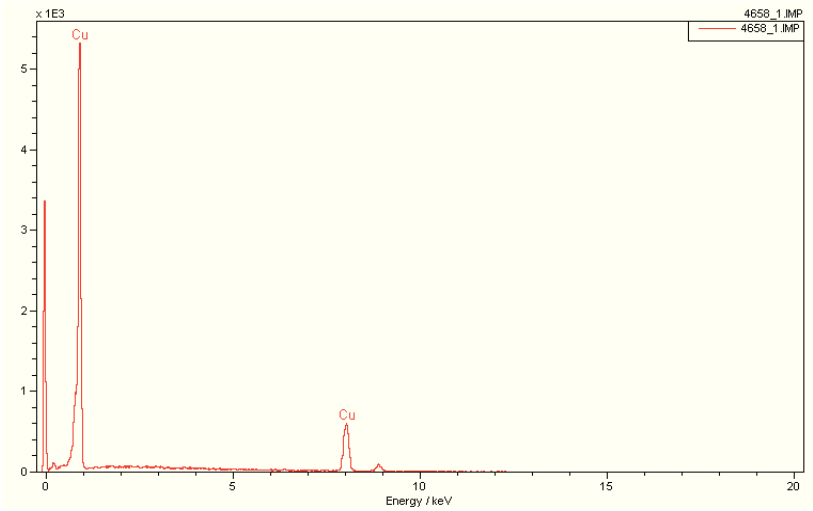

Fig.67 An x-ray energy spectrum obtained from the copper coating - point 1

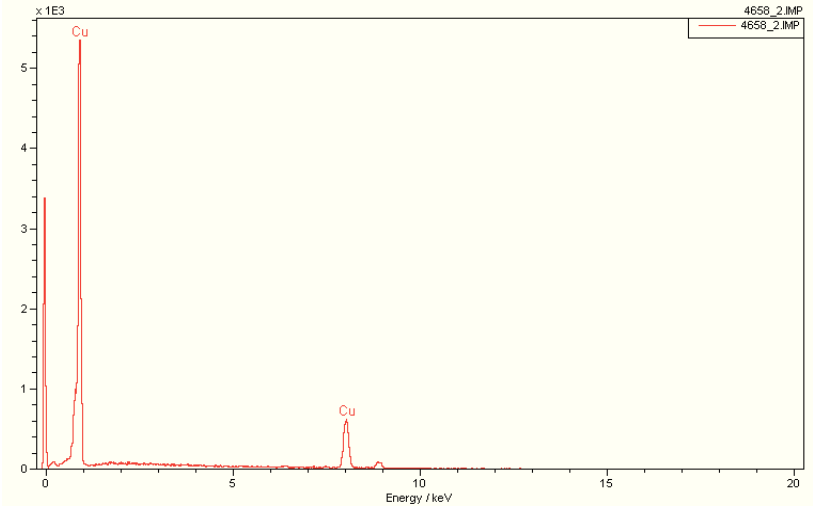

Fig.68 An x-ray energy spectrum obtained from the copper coating - point 2

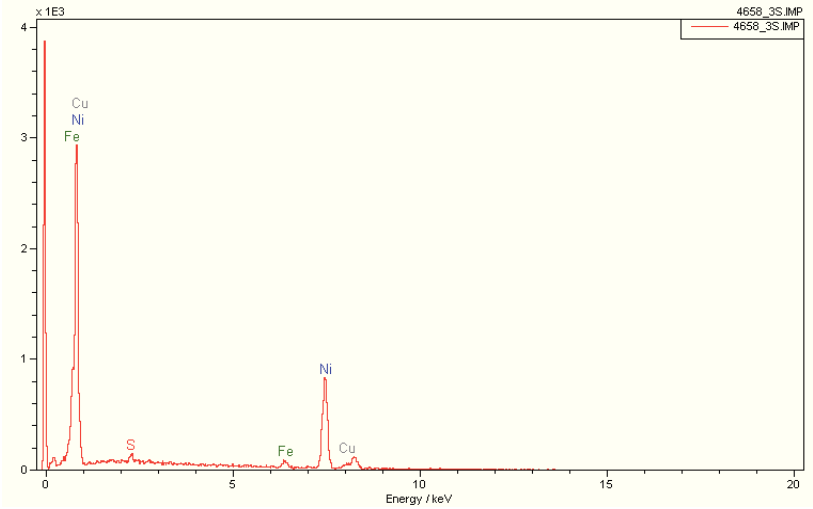

Fig.69 An x-ray energy spectrum obtained from nickel layer - point 3

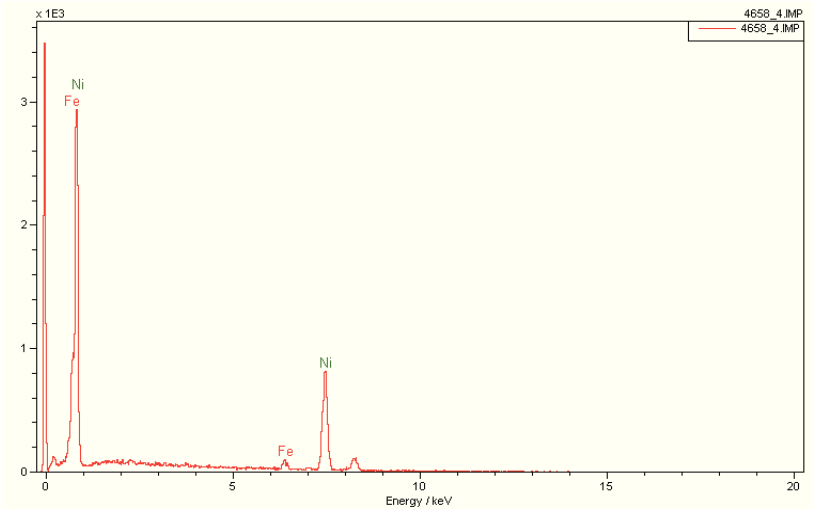

Fig.70 *An x-ray energy spectrum obtained from nickel layer - point 4*

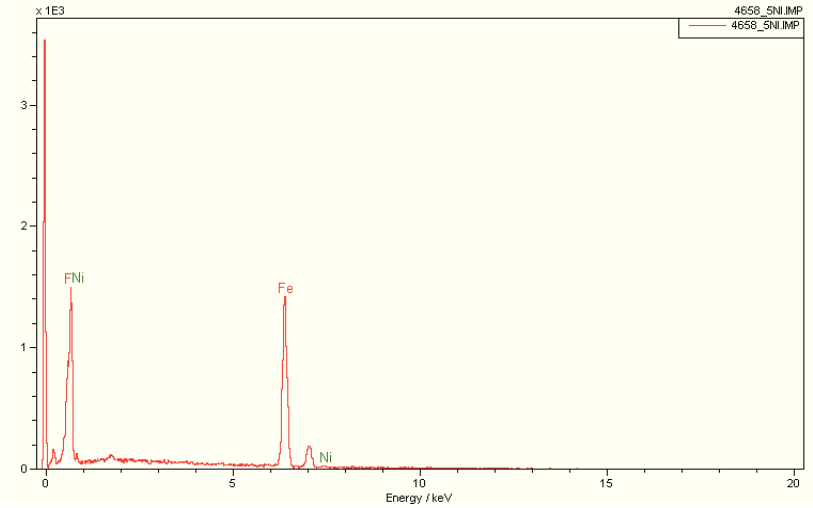

Fig.71 *An x-ray energy spectrum obtained from the steel substrate - point 5*

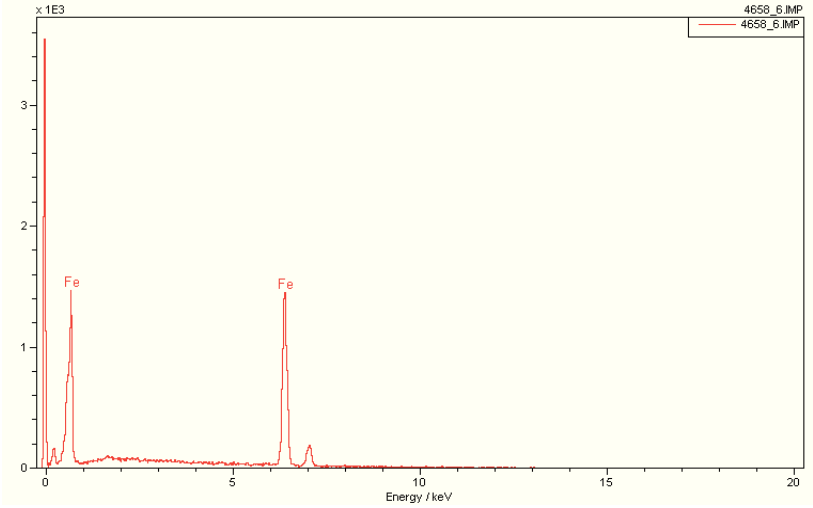

Fig.72 *An x-ray energy spectrum obtained from the steel substrate - point 6*

AN X-RAY MICROANALYSIS SAMPLE WITH A COPPER COATING (Fe//Cup)

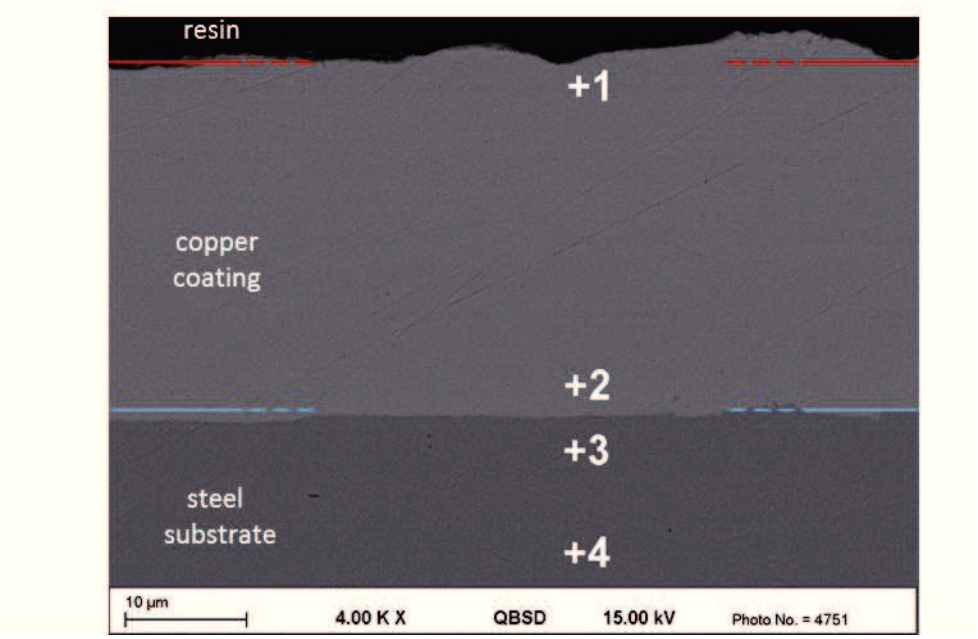

Fig.73 An x-ray microanalysis steel points - point 3,4 and copper coating - point 1,2. 4000x magnification

Table 26 Chemical microanalysis results for a cross section on the border layer copper coating (without sub-layer) - steel substrate (Fe//Cup)

Analyzed element	**Place of analysis**						
	1	2	3	4	5	6	7
	Content in [%] by weight.						
Fe	0,00	1,11	100,00	100,00	-	-	-
Cu	100,00	98,89	0,00	0,00	-		

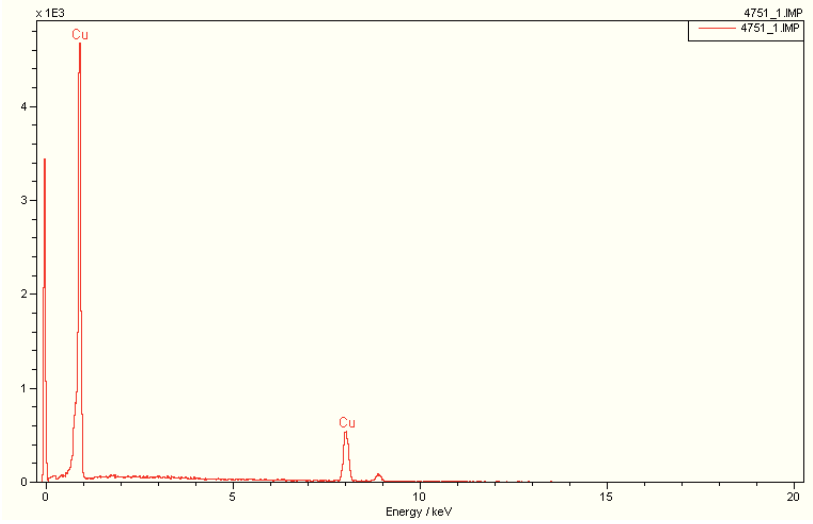

Fig.74 An x-ray energy spectrum obtained from the copper coating - point 1

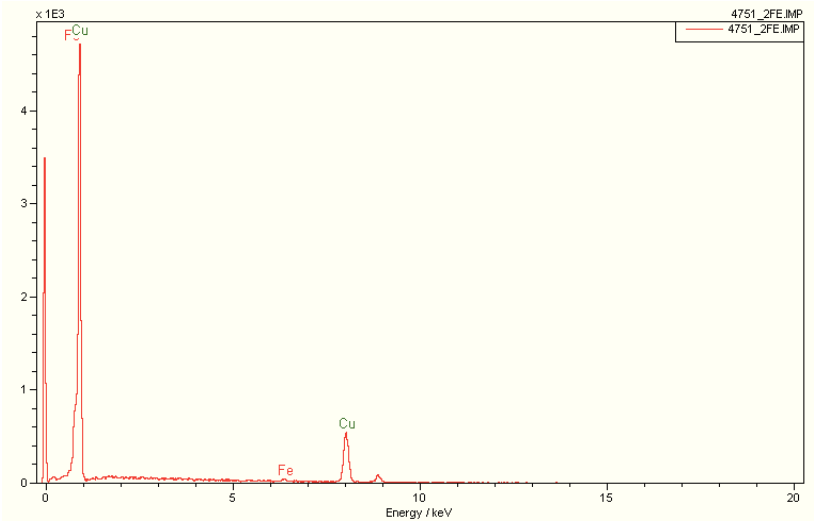

Fig.75 An x-ray energy spectrum obtained from the copper coating - point 2

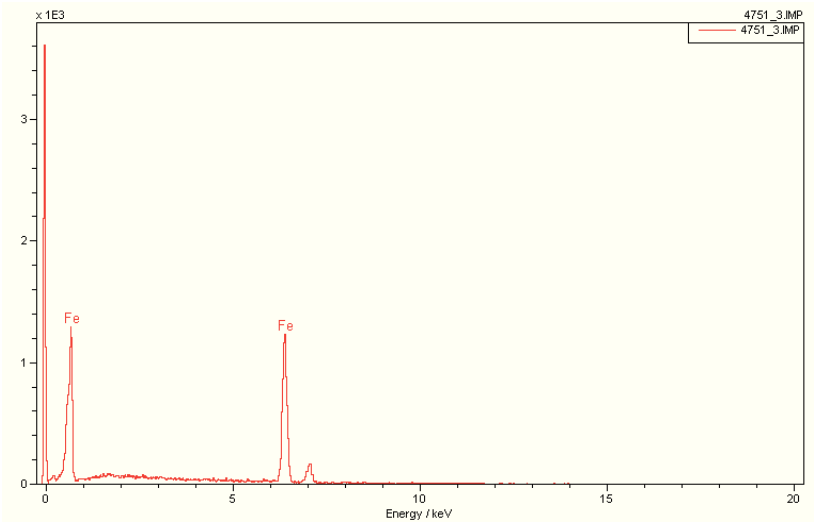

Fig.76 An x-ray energy spectrum obtained from the steel substrate - point 3

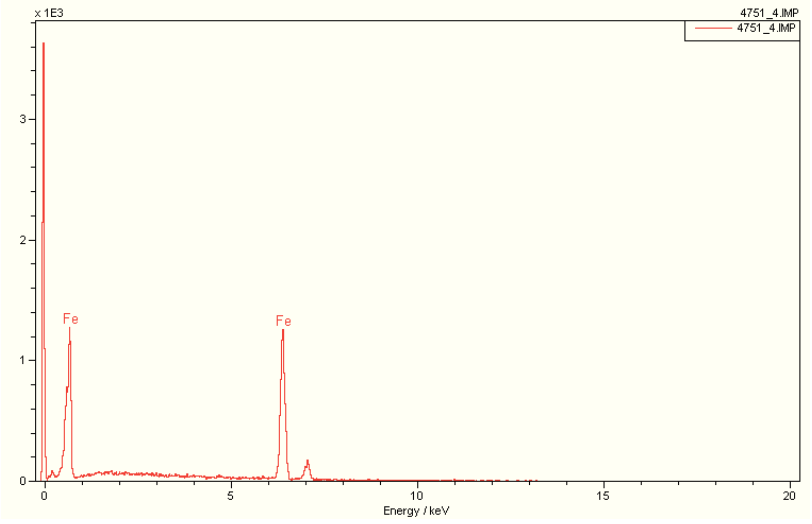

Fig.77 An x-ray energy spectrum obtained from the steel substrate - point 4

8.10 Potentiodynamic corrosion tests

Samples of corrosion resistance with a created metallic coatings were determined using potentiodynamic tests that results in the form of curves of the polarization. It was used in an automated measuring system which comprises of: measuring vessel, potentiostat SI 1286 and a computer (Fig. 78).

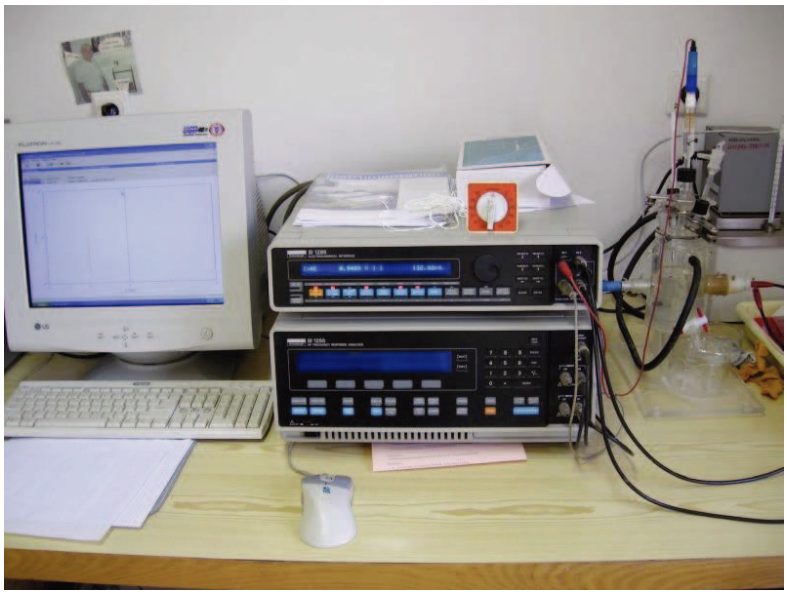

Fig.78 An automated measurement system for electrochemical measurements with a constant current [own investigations]

Polarization curves were recorded in the conventional system of three electrodes. Before starting the measurement, the samples were placed in a corrosive solution (body fluids), in a solution of artificial saliva, artificial blood (SBF-Simulated Body Fluid) and Ringer's solution at 20 ° C for 24 hours. The chemical composition is presented in Table 27. Next they were subjected to the polarization of the potential –1000 mV_{NEK} in the anode direction at a rate of 1 mV/s.

The following notation: E_{kor} - corrosion potential (stationary) samples after 24-hours of exposure to a corrosive solution, $i_{E=-750\ mV}$ - cathodic current density at a potential -750 mV, $E_{K\text{-}A}$ - transition potential cathode-anode, R_p - polarization resistance , i_{kor} - corrosion current density.

Table 27 The chemical composition and sequence of added reagents for the synthesis of body fluids: artificial saliva, artificial blood, Ringer's solution

Component	**Body fluid**		
	Artificial saliva solution	**SBF** (solution artificial blood)	**Ringer's solution (saline solution)**
	Concentration [g/dm^3]		
NaCl	0,700	7,996	8,600
$NaHCO_3$	1,500	0,350	-
KCl	1,200	0,224	0,300
$CaCl_2$	-	-	0,243
$Na_2HPO_4 \cdot 2H_2O$	0,326	0,348	-
$MgCl_2 \cdot 6H_2O$	-	0,305	-
1M HCl	-	47,200	-
$CaCl_2 \cdot 6H_2O$	-	0,549	-
Na_2SO_4	-	0,071	-
$(CH_2OH)_3CHN_2$	-	6,057	-
KSCN (potassium thiocyanate)	0,330	-	-
$CO(NH_2)_2$ (urea)	1,500	-	-

The results of the electrochemical research for DC01 and a multi-layer of metallic coatings electrolytically imposed is presented in the form of a cathodic and anodic polarization curves (Fig. 79 - 86).

The presented results of potentiodynamic and polarization curves graphs obtained, show the differences of material properties (Table 28). Method of preparation (modification) of the surface layer of samples has an effect on the corrosion resistance of the metal layers.

Table 28 The values of corrosion currents and potentials determined for samples with metallic coatings

Body fluid	Number of samples	E_{kor} [mV]	$i_{E=-750\ mV}$ [A/cm^2]	E_{K-A} [mV]	R_p [Ωcm^2]	i_{kor} [A/cm^2]
SBF (solution artificial blood)	**17**	-124	$3{,}40 \cdot 10^{-6}$	-198	$2{,}29 \cdot 10^{5}$	$1{,}14 \cdot 10^{-7}$
	28	-292	$4{,}76 \cdot 10^{-6}$	-322	$1{,}64 \cdot 10^{5}$	$1{,}58 \cdot 10^{-7}$
	37	-193	$4{,}23 \cdot 10^{-6}$	-193	$3{,}11 \cdot 10^{5}$	$4{,}65 \cdot 10^{-8}$
	75	-196	$2{,}21 \cdot 10^{-6}$	-230	$0{,}12 \cdot 10^{5}$	$2{,}18 \cdot 10^{-6}$
Artificial saliva solution	**19**	-249	$1{,}70 \cdot 10^{-6}$	-301	$4{,}93 \cdot 10^{5}$	$5{,}29 \cdot 10^{-8}$
	29	-103	$2{,}82 \cdot 10^{-6}$	-173	$3{,}74 \cdot 10^{5}$	$6{,}98 \cdot 10^{-8}$
	39	-83	$8{,}62 \cdot 10^{-6}$	-327	$0{,}87 \cdot 10^{5}$	$2{,}99 \cdot 10^{-7}$
	76	-137	$6{,}03 \cdot 10^{-6}$	-245	$0{,}84 \cdot 10^{5}$	$3{,}09 \cdot 10^{-7}$
Ringer's solution (saline solution)	**08**	-539	$1{,}07 \cdot 10^{-6}$	-570	$1{,}55 \cdot 10^{5}$	$1{,}68 \cdot 10^{-7}$
	16	-486	$6{,}63 \cdot 10^{-6}$	-494	40703	$6{,}41 \cdot 10^{-7}$
	27	-430	$1{,}71 \cdot 10^{-6}$	-447	$1{,}83 \cdot 10^{5}$	$1{,}43 \cdot 10^{-7}$
	36	-233	$2{,}12 \cdot 10^{-5}$	-250	25070	$1{,}04 \cdot 10^{-6}$
	710	-126	$1{,}79.10^{-5}$	-173	$0{,}29.10^{5}$	$8{,}76 \cdot 10^{-7}$

The drawings below shows the polarization curves for samples 17, 28, 37, 75 (solution artificial blood - SBF) and 19, 29, 39, 76 (solution of artificial saliva) and 08,16,27,36,710 (Ringer's solution) in different combinations coatings after 24 hours of exposure in the corrosion solution.

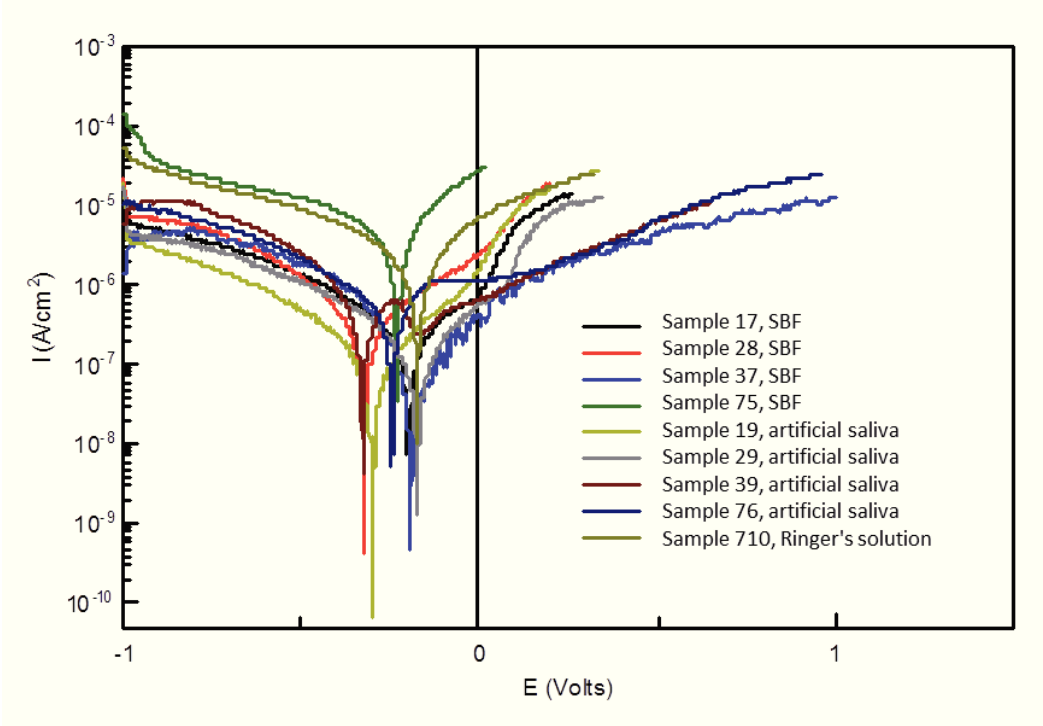

Fig.79 *Polarization curves obtained for the samples of steel with metallic coatings in the corrosion centers*

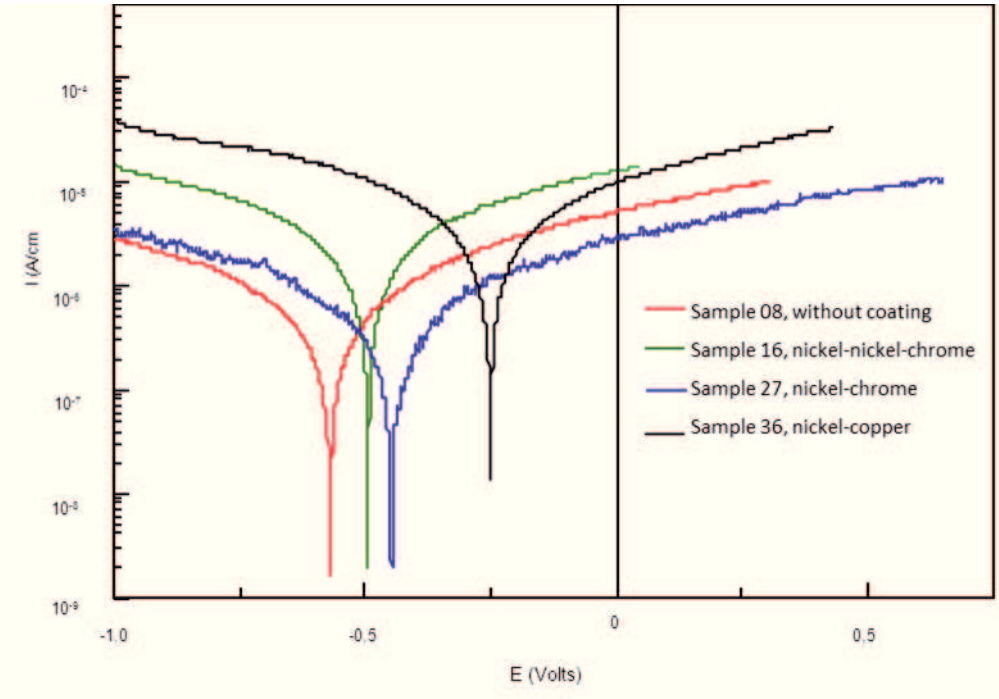

Fig.80 *Polarization curves obtained for samples of steel with imposed metallic coatings in Ringer solution*

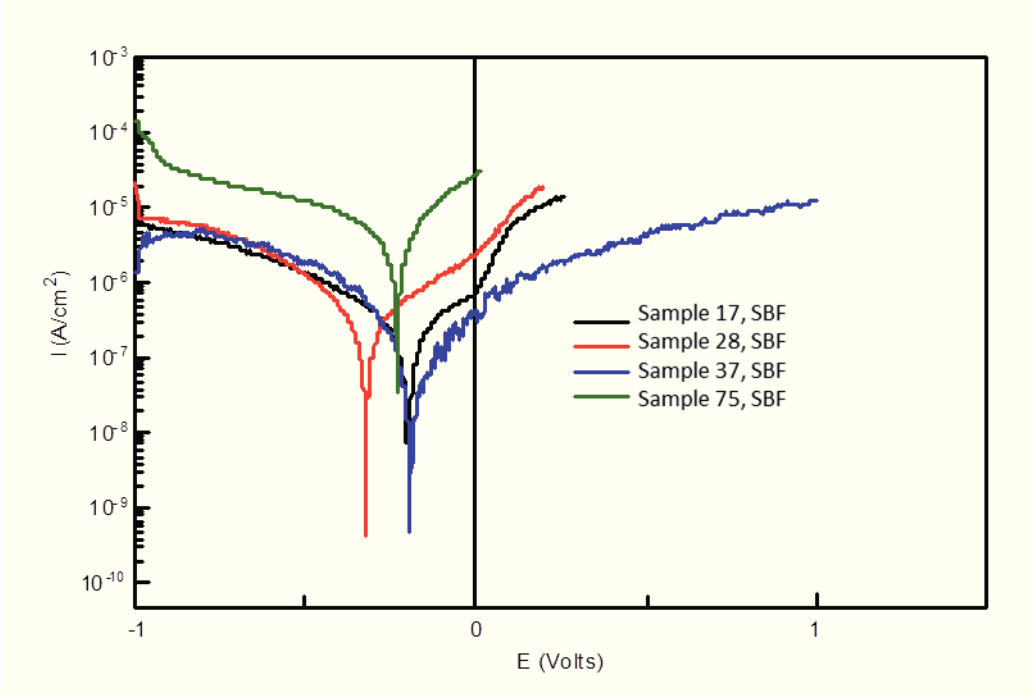

Fig.81 *Polarization curves obtained for samples of steel with imposed metallic coatings in a solution artificial blood - SBF*

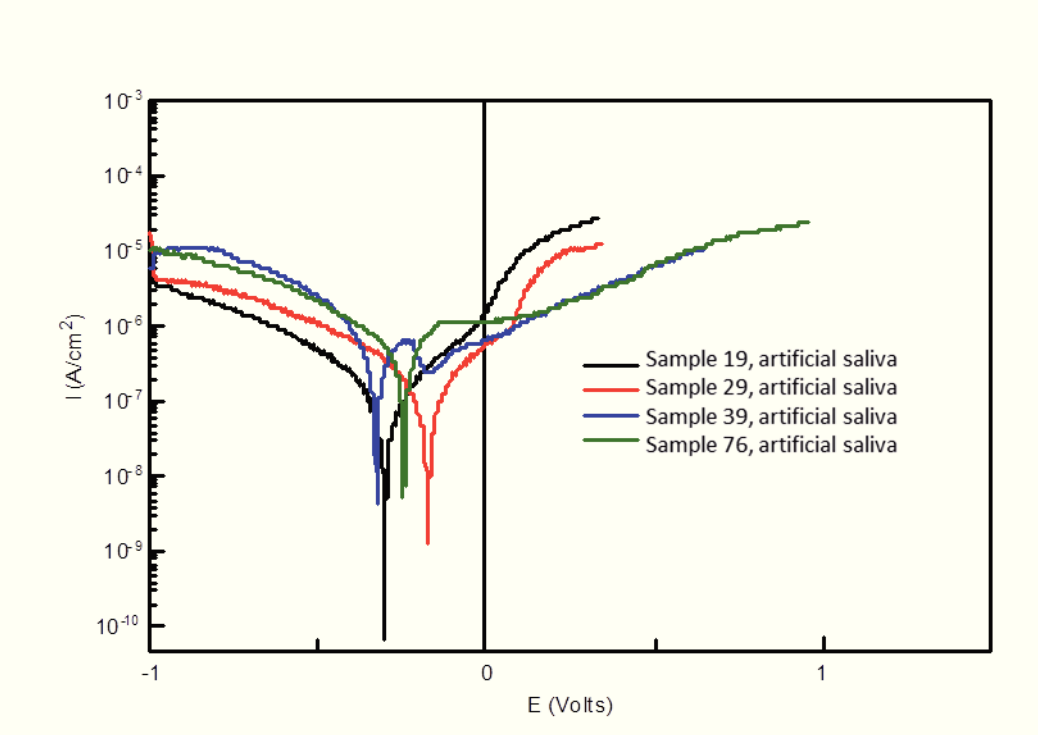

Fig.82 *Polarization curves obtained for samples of steel with imposed metallic coatings in an artificial saliva solution*

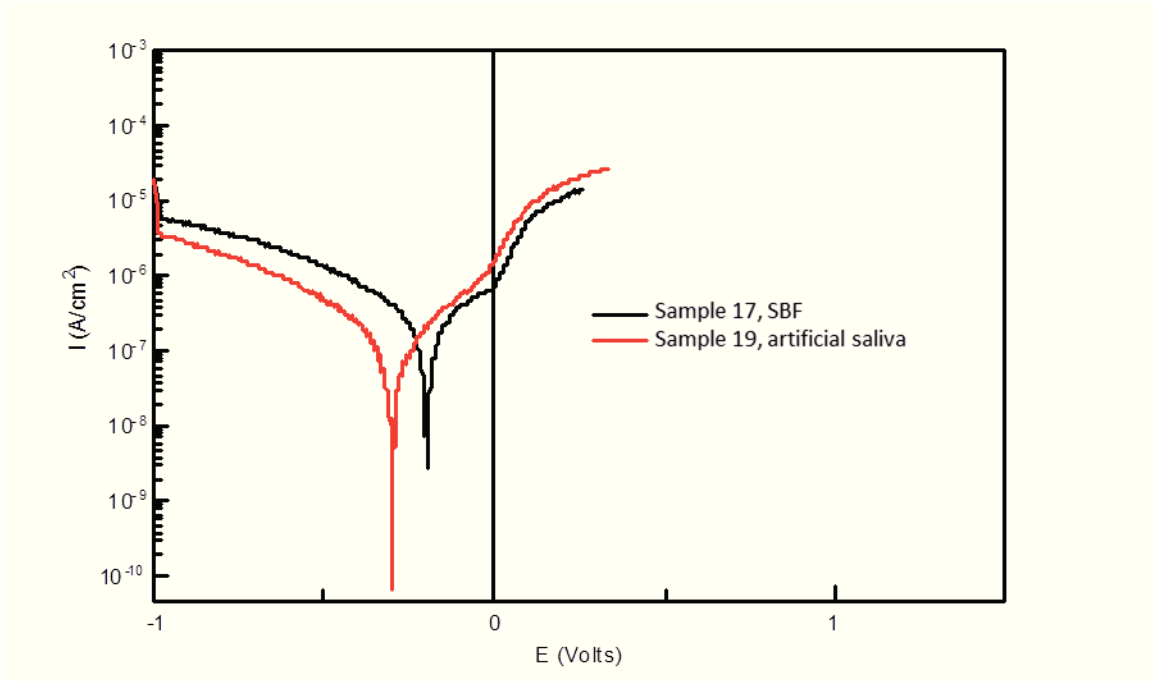

Fig.83 *Polarization curves obtained for the samples of steel with coating nickel-nickel-chrome in the solution artificial blood - SBF and artificial saliva*

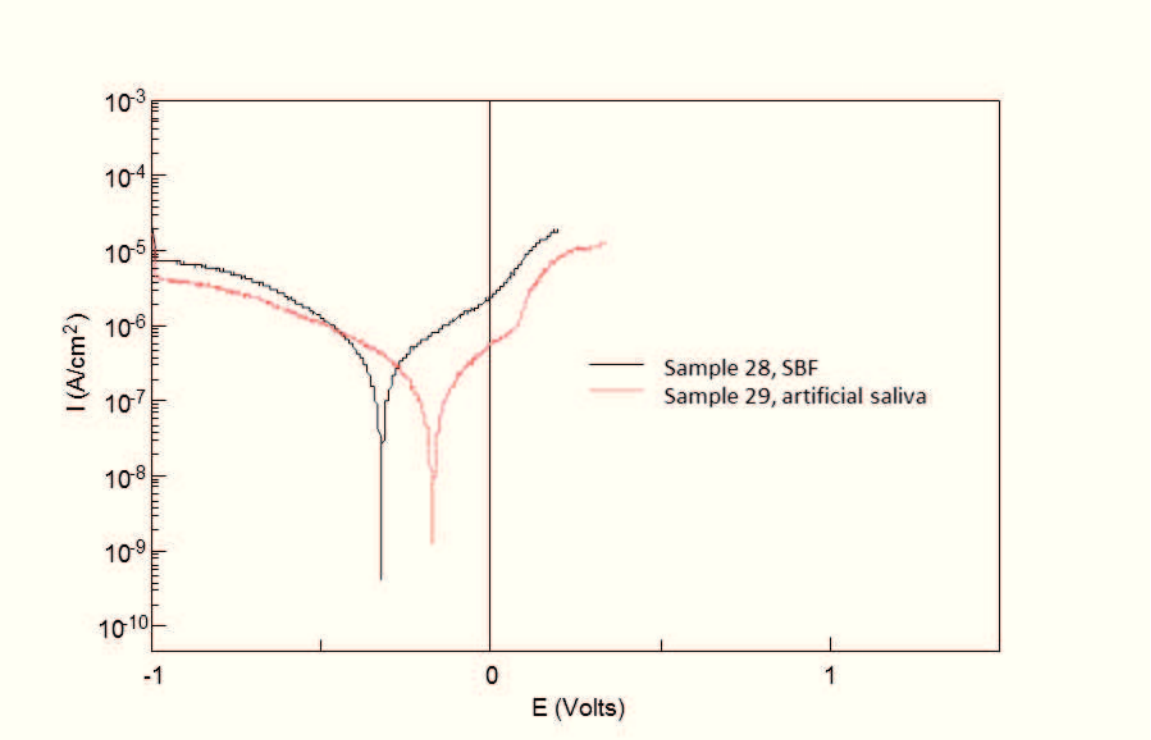

Fig.84 *Polarization curves obtained for the samples steel with coating nickel-chrome in the solution artificial blood - SBF and artificial saliva*

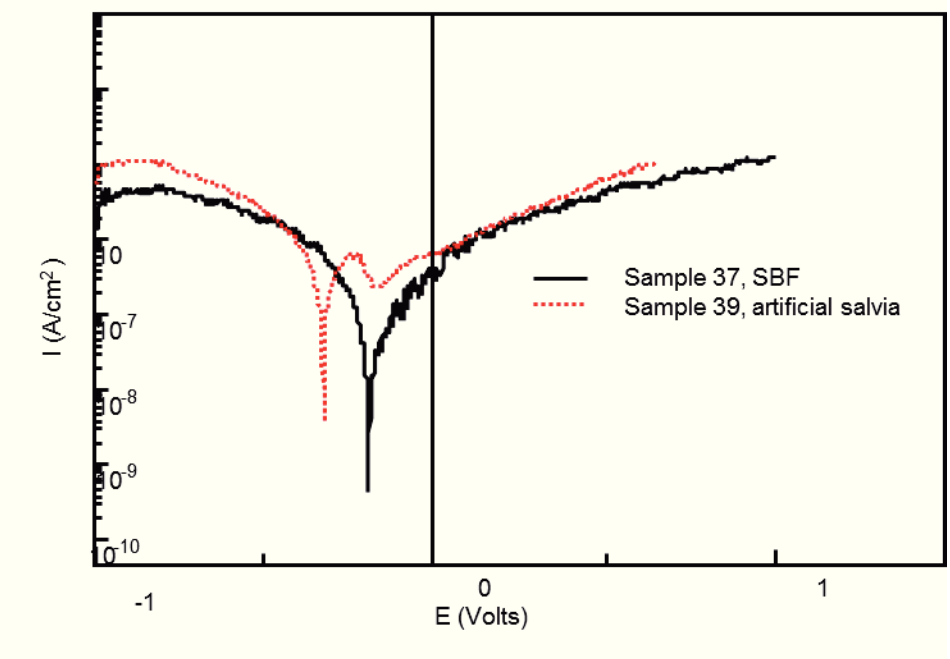

Fig.85 *Polarization curves obtained for the samples of steel with nickel-copper coating in the solution of artificial blood - SBF and artificial saliva*

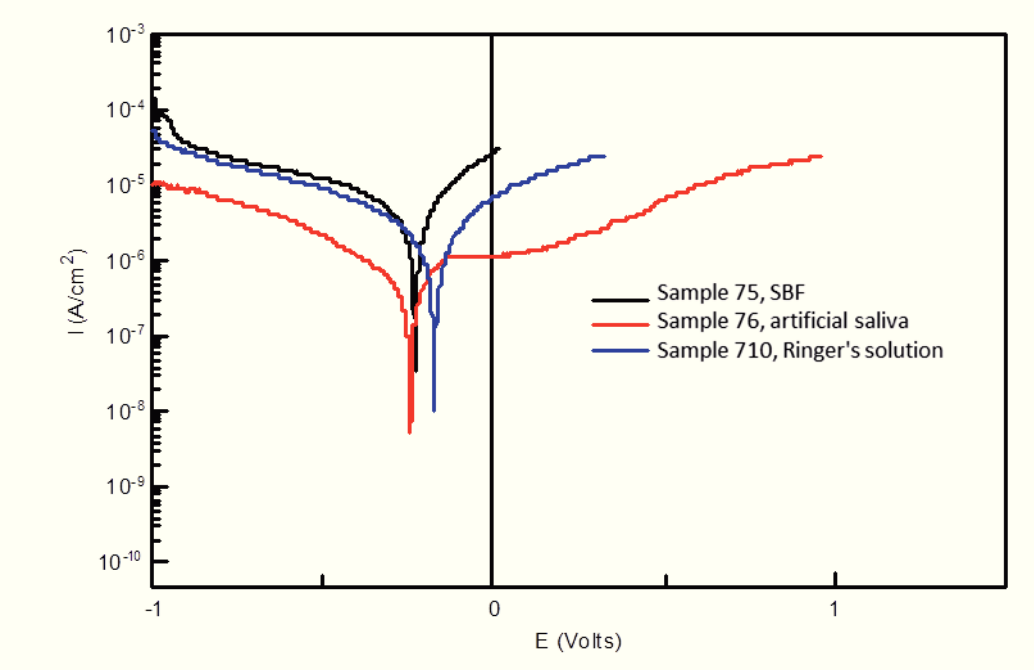

Fig.86 *Polarization curves obtained for the samples of steel with coating copper without a sub-layer in the solution of artificial blood - SBF and artificial saliva*

9 A SUMMARY AND DISCUSSION OF RESULTS

In the literature dealing with the selection of material and surface preparation equipment the design elements, medical equipment dental and peripheral equipment operating rooms have not found any information relating to the sustainability of metallic coatings deposited on the base elements.

The criteria for quality medical specify individual standards based on the recommendations contained in the Act on Medical Products [Journal Polish Set 2010 nr107 pos. 679]. These standards define the structural and functional characteristics of hospital equipment and these are also issues related to applied construction materials (type and quality), and protective coatings.

- An analysis of the chemical composition of the steel DC01 (the geometry of the disc) and RSt37-2 NBK (the geometry of the pipe) (Tab.7) for analysis confirmed the compliance with standards and specifications submitted by the supplier. The hardness tests showed little difference between the two steel grades. Was respectively DC01 106 HV1 and for RSt37-2 NBK 140 HV1. Metallography microscope research material indicates that it is a fine-grained steel structure typical of the products cold-rolled low-carbon steel, unalloyed steel for cold working.

- The adopted standard preparation of the test material is consistent with the technology which spaces design elements prepared under the galvanic treatment of the manufacturing plant of medical equipment.

- In the assessment of the surface layer of the samples before the imposition, galvanic coatings must be observed so that the geometry of the sample pipes have a higher degree of development of the surface (Ra 0,18 µm) than the samples of geometry disk (Ra of 0,10 µm). In terms of the surface the 3D of the disc emerged many inequalities in the form of single peaks arising after the process of preparing the surface by grinding and polishing (Fig. 32). A profile of the pipe surface in terms of the 3D to participate is permanent and has only had a few inequalities registered in the form peaks (Figure 33).

The curve participation of the material informs that the profile surface of the disc has a larger share coefficient Mr1 (elevations protruding from the roughness core profile), which was 9,20%, compared to the pipe - Mr1 5,82%. inequality. However coefficient Mr2 (deep valley of the roughness core profile) for the profile of the pipe amounted to 92,23 %. It

follows from this that the grinding with polishing the samples in the form of disc gave more (continuous) a flat surface - Mr2 87,91% (Fig. 32, 33).

- Protective coatings metallic type nickel-nickel-chromium, nickel-chromium coatings are used as a standard on the hospital medical equipment. The exception is the coatings nickel-copper and copper which, because of the low aesthetic values and low protective properties, are not commonly used. Metallographic tests thickness layers of metallic coatings for the disc showed that the average thickness of the coating nickel-nickel-chrome is 24,0 μm, nickel-chrome 13,5 μm (Fig.47). Fulfills the conditions of the standards relating to the requirements that apply to the hospital conditions. Samples with nickel-copper (13,5 μm coating thickness)and copper coating (29,7 μm coating thickness) (Fig.48) are not found in the Polish Standards, and the measured values showed that the thickness of the coating is similar to the thickness with a surface layer of chromium.

A coating thickness for samples with a pipe geometry amounted for the coatings: nickel-nickel-chrome 49,0 μm, nickel-chrome 42,7 μm, nickel-copper 17,0 μm and copper 24,7 μm (Fig. 49, 50). This case in the assessment of the surface layer before and after the imposition of galvanic coatings shows a slightly adjusted surface profile (raw - Ra 0,18 μm, nickel-nickel-chrome coating - Ra 0,14 μm, nickel-chrome coating - Ra 0,17 μm).

The resulting coatings nickel-nickel-chromium and nickel-chrome is a significant thickness in relation to the geometry of the disc sample was intended in-order to demonstrate an absence of difference in the adhesion to the steel substrate.

- The research stereo-metric disc geometry samples performed after the imposition of the metallic coatings indicate that the surface layer has been development in relation to the samples in the initial state (Ra 0,10 μm, Fig. 32). Copper coating (without sublayer) with Ra 0,24 μm has the largest roughness coefficient (Fig. 38). For other samples with coatings nickel-nickel-chrome (Ra 0,14 μm), nickel-chrome (Ra 0,11 μm), nickel-copper (Ra 0,12 μm) there has been a slight increase in the average roughness factor 0,02 μm (Fig. 35 , 36, 37).

The surface layer samples profile the pipe with coatings nickel-nickel-chrome (Ra 0,14 μm), nickel-chrome (Ra 0,17 μm), nickel-copper (Ra 0,18 μm) and it was slightly "micro-smohing" ("healed surface") (Fig. 38, 39, 40). Preserves the surface layer of a similar nature in relation to the initial state - Ra 0,18 μm (Figure 32). The surface layer of the copper coating (without sublayers) - Ra 0,27 μm, has been similarly as in the case of the sample in the form of a disk which has been significantly development (Fig. 42).

- The x-ray microanalysis points of the samples showed the disc profile chemical composition of the individual galvanic layers and the substrate.

On the cross section the layers of the sample with coating nickel-nickel-chrome and nickel-chrome indicated that a chromium layer with a thickness of 0,4 μm is too thin to perform any accurate measurements. Accuracy of measurement for an x-ray microprobe is 1 micrometer. Attesting to this is shown in the presence of Ni, Ca, Cu, Al, S, Si, which comes from layers adjoining to the layer of chromium (Tables 24 and 25).

Energy spectra obtained from the nickel layers for all the samples showed trace amounts of flat iron which indicates contamination of the bath nickel ions of iron (III). The phenomenon of contamination nickel ions iron bath is a natural process, but the contamination has its limit values and it is 50 mg/dm^3.

The analysis micro-area points for the glossy copper layer (sample with coating nickel-copper) for two measuring points 1 and 2 showed no additives other than metallic elements. The presence of nickel in the ground is noticeable on the border of the substrate - a layer of point 5. This may indicate the single migration of nickel ions in the surface layer of the substrate (Fig. 66, Tab. 25).

In the layer of copper matte (a sample of copper without a sub-layer) recorded a presence of Fe on the border of the substrate with a layer of copper - measuring point 2 (Fig. 73, Tab. 26). The reason for this may be the emergence of a complex cyanides of iron in a cyanide bath, informing about the contamination.

- Potentiodynamic tests for samples with the geometry of the disc indicates that the body fluids have a different aggressiveness with respect to the metallic coatings. The potential of the metal is a measure of its "nobility" in the electrolyte. The higher the value of the corrosion potential the greater "nobility of" metal.

The surface modification coating nickel-nickel-chromium, nickel-chromium, nickel-copper and copper resulted in a change of E_{kor} - corrosion potential.

It was found that the lowest E_{kor} (-539 mV) shows a sample No. 08 (without modification) in Ringer solution - Table 28.

The use of coatings on steel resulted in an increase of Ekor modified samples. The highest increase of E_{kor} relative to an unmodified surface of the substrate has a sample 39 (nickel-copper) by more than 456 mV. In comparison to the other coatings its nickel-copper coating has the highest values E_{kor}.

The lowest E_{kor} potential (- 486 mV) in Ringer solution for coatings applied showed sample 16 (nickel-nickel-chromium).

Exposure of samples (24 hours) in body fluids resulted in a change in the cathode current density at a potential -750 mV - ($i_{E= -750\ mV}$). The observed changes can be explained by the change of speed of the electrode processes occurring on the surface of the substrate and the coating. These changes indicate that the modified surface of the substrate affects the current density of the cathode at a potential -750 mV ($i_{E= -750\ mV}$)

The highest value ($i_{E=-750mV} = 2{,}12 \cdot 10^{-5}$ A/cm^2) with respect to the substrate ($1{,}07 \cdot 10^{-6}$ A/cm^2) as well as the remaining coatings shows sample No. 36 (nickel-copper) in Ringer's solution. This layer behaves similarly in the artificial saliva solution as in the artificial blood.

Changing the potential transition cathode - anode (E_{K-A}) shows the dynamics of electrode processes occurring at the boundary metal phase- the body fluid.

The measured values of the potential transition cathodic - anode $E_{K–A}$ the substrate without the coating and in various security configuration metallic coatings in Ringer's solution after a 24-hr exposure which indicates that the type of coating used to move the $E_{K–A}$ in the direction of the more positive values of about 320 mV. The reason for this is to form a layer containing the appropriate barrier properties. For artificial blood the highest potentials transition of cathodic - anode with similar values (198 mV and-193 mV) was recorded for coating nickel-nickel-chromium and nickel-copper. The artificial saliva highest potential ($E_{K–A}$= -173 mV) shows a sample of nickel-chrome coating.

Polarization resistance R_p shows the nature of the activity of body fluids. The observed changes in polarization resistance due to the difference in the chemical composition of the coating. The exposure (24 hours) modified substrate showed that the highest resistance R_p ($4{,}93 \cdot 10^5$ Ωcm^2) reached nickel-nickel-chromium coating in the artificial saliva solution, whilst the lowest value of the polarization resistance ($1{,}20 \cdot 10^4$ Ωcm^2) has a copper coating without a sub-layer in the artificial blood solution.

The measurement of the corrosion rate to any metal in a corrosive environment is the corrosion current density i_{kor} . The higher the density the more quickly i_{kor} corrosion processes follows under any given circumstances.

The highest corrosion rate ($i_{kor} = 1{,}18 \cdot 10^{-6}$) found for copper coating without a sub-layer of solution of artificial blood. However, the slowest ($i_{kor} = 4{,}65 \cdot 10^{-8}$) corrosion process occurred in a solution of artificial blood for nickel-copper coating. This confirms therefore that a high degree of development of the surface layer negative effect on the corrosion

resistance of the coating. For copper coating without a sub-layer the roughness coefficient Ra of 0,24 μm, is twice as high as the other coatings.

In summary, potentiodynamic research showed that the most resistant of the coating to the effects centers corrosive are coatings, which have the lowest degree development of surface layer and they are: for artificial blood - nickel-copper coating ($i_{kor} = 4{,}65 \cdot 10^{-8}$) for artificial saliva solution - nickel-nickel-chrome coating ($i_{kor} = 5{,}29 \cdot 10^{-8}$), for Ringer's solution is a nickel-chrome coating ($i_{kor} = 1{,}43 \cdot 10^{-7}$) - Table 28.

10 SOCIAL BENEFITS

Social benefits doctoral dissertation in the field of medical equipment protection from corrosion is shown in the following points:

- A high degree of development of the surface layer of the protective coating which has a negative effect on the corrosion resistance is an example of a copper coating without sub-layers with the highest roughness factor of 0,24μm, this confirms the effect of roughness on the corrosion resistance despite the fact that the coating was the thickest coating of 29,7μm from among the tested;

- maintaining a continuity of coatings with a low coefficient of roughness improves the corrosion resistance of the coating refers to nickel - nickel – chrome 0,14 μm, nickel-chromium 0,11 μm and nickel-copper 0,12 μm;

- economic aspects

- the application of metallic coatings with a surface layer of copper of a high gloss and low coefficient of roughness will increase corrosion resistance,
- application of a coating of a surface layer of copper will contribute significantly to a decrease in the number of people hospitalized who are re-infected in hospitals,
- copper has antibacterial properties, which ensure the maintenance of medical equipment in aseptic conditions;

- environmental aspect

- the application of protective coatings with very low coefficient of roughness enable longer life medical equipment.

11 CONCLUSIONS

Protective coatings metallic found in hospitals are mostly coatings type nickel-chrome. The reason for using this type of coatings is it is easy to maintain aseptic medical devices. However, the continuity of how and the low roughness of such a coating is a guarantee to maintain high standards of hygiene in hospital conditions.

The research is focused on the selection of coating which would meet the expectations users of medical equipment both in terms of corrosion resistance and antibacterial.

The object of research was the bed rehabilitation, where local corrosion was found. The corrosion products contain a many elements indicating the cause of the destruction of the coating. The identified elements calcium, chlorine, potassium, carbon, sodium, aluminum, magnesium, sulfur, are components of body fluids blood, saliva, of meals remnants, but also of disinfectants Conducted observations exploited medical equipment in hospital conditions confirmed the existence of this type of pollution on protective coatings.

The appearance of corrosion is also a health hazard or even life threatening to patients with reduced immune resistance. Because it has been shown that corrosion is a good place for locating dangerous strains of bacteria and fungi.

The application of metallic coatings with a surface layer of copper of a high gloss and low coefficient of roughness will increase corrosion resistance.

The application of a coating of a surface layer of copper will contribute significantly to the decreases in the number of people hospitalized who are re-infected in hospitals.

Copper has antibacterial properties, which ensure the maintenance of medical equipment in aseptic conditions.

The applications of protective coatings with very low coefficient of roughness enable longer life medical equipment.

Light of the foregoing selecting a coating of nickel-copper is the best solution for the protection of medical equipment from corrosion and also an excellent antibacterial protection in the context of protection of human health of hospitalized.

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DIN 50960-1Eelectroplated and chemical coatings; designation and specification in technical documents

ISO 4539:1980 Electrodeposited chromium coatings. Electrolytic corrosion testing (EC test)

PN-H-04615:1984 Corrosion of metals -- Laboratory test by the thioacetamide procedure. Standard withdrawn from circulation and replaced by PN-EN ISO 4538:2001

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PN-EN 10130:2009Cold rolled low carbon steel flat products for cold forming - Technical delivery conditions

PN-EN 1403:2002 Corrosion protection of metals - Electrodeposited coatings - Method of specifying general requirements

PN-EN ISO 10062:2008
Corrosion tests in artificial atmosphere at very low concentrations of polluting gas(es). Standard withdrawn from circulation and replaced by PN-EN ISO 10062:2009

PN-EN ISO 13565-1:1999Geometrical product specifications (GPS) - Surface texture: Profile method - Surfaces having stratified functional properties - Part 1: Filtering and general measurement conditions (ISO 13565-1:1996)

PN-EN ISO 13565-2:1999Geometrical product specifications (GPS) - Surface texture: Profile method - Surfaces having stratified functional properties - Part 2: Height characterization using the linear material ratio curve (ISO 13565-2:1996)

PN-EN ISO 13565-3:2002Geometrical Product Specifications (GPS) - Surface texture: Profile method - Surfaces having stratified functional properties - Part 3: Height characterization using the material probability curve (ISO 13565-3:1998)

PN-EN ISO 1456:2009 Metallic and other inorganic coatings - Electrodeposited coatings of nickel, nickel plus chromium, copper plus nickel and of copper plus nickel plus chromium (ISO 1456:2009)

PN-EN ISO 3274:2011Geometrical product specifications (GPS) - Surface texture: Profile method - Nominal characteristics of contact (stylus) instruments (ISO 3274:1996)

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